ORGANOMETALLIC CHEMISTRY OF TRIOSMIUM CLUSTERS

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Declaration

The research described herein was conducted by the author at The Department of Chemistry, The University of Edinburgh, between the dates of October 1991 and December 1994. It is the author's original work unless specific reference is made to the contrary. None of the work described herein has been submitted for a degree at any other institution.

Jacqueline G. M. Nairn

In memory of my mother

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Chapter 3: A route to a *bis*-benzene triosmium cluster

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Abstract

The interaction of transition metal carbonyl clusters with unsaturated cyclic and polycyclic ligand systems continues to stimulate ongoing research and this thesis is concerned mainly with the reactions of triosmium carbonyl clusters with such compounds.

Chapter one contains a brief summary of triosmium dodecacarbonyl chemistry, incorporating both synthesis and reactivity. The arene chemistry of mononuclear complexes and cluster compounds is also discussed. Over the last decade there has been serious debate on the validity of the cluster-surface analogy; the boundary conditions are addressed herein.

Chapter two details alternative synthetic routes to the compound $M_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$ [M= Ru, Os]. A series of substituted 1,3-cyclohexadiene ligands have also been prepared and reacted with the cluster $Os_3(CO)_{10}(MeCN)_2$.

The successful synthesis of the *bis*-benzene cluster $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^6{-}C_6H_6)$ is reported in chapter three. The systematic stepwise reaction of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$ with trimethyl amine-N-oxide and 1,3-cyclohexadiene leads to the formation of a range of benzene-diene clusters, all of which have been fully characterised. Their isomeric and fluxional behaviour has also been studied.

The reactions of acenaphthylene, $C_{12}H_8$, a stable tricyclic system with 12π-electrons available for bonding, are reported for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in chapter four. The resulting compounds demonstrate the range of bonding modes adopted by this flexible ligand.

Chapter five reports the experimental procedures and instrumentation used and includes spectroscopic and crystallographic data.

Glossary of abbreviations

IR	Infra-red
υCO	carbonyl stretching frequency
s	strong
m	medium
w	weak
sh	shoulder
br	broad
vs	very strong
nmr	nuclear magnetic resonance
δ	chemical shift
ppm	parts per million
Hz	hertz
s	singlet
d	doublet
dd	doublet of doublets
t	triplet
m	multiplet
MS	mass spectroscopy
amu	atomic mass units
FAB	fast atom bombardment
nOe	nuclear Overhauser effect
L	ligand
R	alkyl or aryl
Me	methyl
Et	ethyl
Ph	phenyl
THF	tetrahydrofuran
***Cp**	pentamethylcyclopentadiene
DBU	1,8, diazobicyclo[5.4.0]undec-7-ene
COT	cyclooctatetraene
tlc	thin layer chromatography

Numbering of compounds

$Os_3(CO)_{12}$	**1**	
$Ru_3(CO)_{12}$	**2**	
$Os_3(CO)_{10}(MeCN)_2$	**3**	
$Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	**4**	
$Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	**5**	
$Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$	**6**	
$Fe(CO)_3(o\text{-}Me_2C_6H_6)$	**7**	
$Os_3(CO)_{10}(\eta^4\text{-}o\text{-}Me_2C_6H_6)$	**8**	
$Fe(CO)_3(p\text{-}Me_2C_6H_6)$	**9**	
$Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$	**10**	
$Fe(CO)_3(m\text{-}Me_2C_6H_6)$	**11**	
$Os_3(CO)_{10}(\eta^4\text{-}m\text{-}Me_2C_6H_6)$	**12**	
$Fe(CO)_3(MeC_6H_7)$	**13**	
$Os_3(CO)_{10}(\eta^4\text{-}MeC_6H_7)$	**14**	
$Fe_2(CO)_6(C_{14}H_{18})$	**15**	
$Os_3(CO)_{10}(\eta^4\text{-}C_{14}H_{16})$	**16**	
$Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)$	**17**	
$Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$	**18**	
$Os_3(CO)_{11}(\eta^2\text{-}CH_2CH_2)$	**19**	
$Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$	**20**	
$Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$	**21**	*'equatorial-axial'*
$Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$	**22**	*'bis-equatorial'*
$H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$	**23**	
$Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$	**24**	
$[Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$	**25**	
$H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$	**26**	
$Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}o\text{-}Me_2C_6H_6)$	**27**	
$Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}p\text{-}Me_2C_6H_6)$	**28**	
$Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}p\text{-}Me_2C_6H_6)$	**29**	
$Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$	**30**	
$H_2Os_3(CO)_9(C_{12}H_6)$	**31**	
$Os_6(CO)_{18}$	**32**	
$HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$	**33**	
$Os_2(CO)_6(C_{12}H_6)_2$	**34**	
$[Os_3(CO)_9(C_{12}H_6)]^{2-}$	**35**	
$^*CpRhOs_3(CO)_9(C_{12}H_6)$	**36**	

Chapter 1:- Introduction

This chapter commences with a brief summary of the chemistry of triosmium dodecacarbonyl, incorporating the synthesis and reactivity of $Os_3(CO)_{12}$ and some activated derivatives. Several examples of arene sandwich complexes are reported followed by an introduction to arene cluster chemistry, concentrating mainly on the η^6-terminal and the μ_3:η^2:η^2:η^2-face capping co-ordination modes in a range of transition metal carbonyl clusters. Finally the analogy between metal surfaces and clusters is addressed, focusing closely on the boundary conditions that must be considered. A comparison of the chemisorption of benzene on a flat metal surface with the bonding observed in carbonyl clusters is also discussed.

1.1 Triosmium dodecacarbonyl: Synthesis and reactivity

1.1.1 Introduction

The compound $Os_3(CO)_{12}$ was first reported by Hieber and coworkers in 1943.[1] Although initially formulated as $Os_2(CO)_9$, analogous to $Fe_2(CO)_9$, the trimeric nature of the compound was later established.[2] The initial synthesis involved the reaction of OsO_4 with HI to give an oxyiodide compound which when treated with silver powder in benzene at 150°C under CO(200atm) afforded $Os_3(CO)_{12}$ in poor yields . However, it was the improved synthetic routes reported in 1967[3] and 1968[4] that marked the beginning of triosmium chemistry. The solid state symmetry of triosmium dodecacarbonyl is approximately D_{3h}, with the six axial and six equatorial CO ligands defining a cube-octahedron.[5] Competition between axial ligands for metal π-electron density results in the M-C bond lengths being slightly longer and the C-O bonds shorter than the equatorial CO groups. The crowding of the axial ligands limits substitution at an axial co-ordination site to only simple rod-like ligands or hydrides.

The chemistry of $Os_3(CO)_{12}$ has been extensively studied. This is due in part to the diamagnetic, air-stable, inertness of most Os_3 compounds which can be easily handled in air, crystallised and characterised. Interest also stems from their relation to the chemisorbed species. The formation of the μ_3-ethylidyne ligand in $H_3Os_3(CCH_3)(CO)_9$[6], from the reaction of $Os_3(CO)_{12}$ with ethylene *via* a $H_2Os_3(C{=}CH_2)(CO)_9$ intermediate, parallels the formation of CCH_3 on a Pt(111) surface.[7] Similarly the identification of μ_3-CHCH on Pt(111) and Pd(111) surfaces has been achieved by a comparison of the vibrational spectra of the chemisorbed species

with that of the cluster $Os_3(\mu_3\text{-}C_2H_2)(CO)_{10}$.[8] The validity of the analogy between clusters and surfaces will be broached in section 1.3.

1.1.2 Changes in nuclearity

When subjected to high temperatures $Os_3(CO)_{12}$ losses CO and cluster build up is observed. At 210°C, the major product obtained is $Os_6(CO)_{18}$, however, small amounts of $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ can also be isolated.[9] Pyrolysis at higher temperatures leads to the formation of carbido species, such as $Os_8C(CO)_{21}$ and $Os_5C(CO)_{15}$. The carbido ligand results from the reduction of a carbon monoxide group.[10] The cluster $Os_6(CO)_{18}$ may also be obtained by the partial reduction of $Os_3(CO)_{12}$ using Na in diglyme at 162°C. The dianion $[Os_6(CO)_{18}]^{2-}$ is formed , probably by a condensation reaction between $[Os_3(CO)_{11}]^{2-}$ and $Os_3(CO)_{12}$. Oxidation of the dianion with Fe(III) forms $Os_6(CO)_{18}$.[11] Heating $Os_3(CO)_{12}$ in hexane under H_2 pressure yields $H_4Os_4(CO)_{12}$[12], while similar treatment with C_2H_4 gives $H_2Os_3(C{=}CH_2)(CO)_9$ and small amounts of the clusters $Os_4(CO)_{12}(CH{=}CH)$ and $Os_4(CO)_{12}(CH{=}CEt)$.[13] The building of high nuclearity clusters is often facilitated by the use of strongly bridging ligands such as sulphur. Direct reaction of $Os_3(CO)_{12}$ with sulphur at 260°C has been shown to yield $Os_3(S)_2(CO)_9$, $Os_5(S)(CO)_{15}$, $Os_6(CO)_{18}$ and $Os_{10}(S)_2(CO)_{23}$.[14]

Ultra violet photolysis of $Os_3(CO)_{12}$ in the presence of dienes such as butadiene[15] and cyclooctadiene[16] leads to the formation of mononuclear species of the type $Os(CO)_3$(diene). Dinuclear osmium(I) compounds of the type $Os_2(\mu\text{-}X)_2(CO)_6$ have been synthesised by the oxidation of $Os_3(CO)_{12}$ with X_2 (X=Cl,Br). The high temperature treatment of $Os_3(CO)_{12}$ with various reagents initially forms trinuclear species. However, these compounds can be broken down at higher temperatures. This process has been demonstrated in section 4.5 in the reaction of $Os_3(CO)_{12}$ with acenaphthylene, where the dinuclear compound $Os_2(CO)_6(C_{12}H_6)_2$ can be successfully obtained from the thermolysis of the trinuclear complex $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$. Reactions leading to mono- or di-nuclear species are much rarer for $Os_3(CO)_{12}$ than for $Ru_3(CO)_{12}$, where cluster breakdown is often observed. This reflects the increased bond energy of the metal-metal bond on descending the triad.

1.1.3 Displacement reactions

The main preparative methods employed initially in the synthesis of substituted triosmium clusters involved either thermal or photochemical activation of the cluster. As anticipated, with many reagents these methods of activation lead to a mixture of

products, although in most cases they can be separated by chromatographic techniques. Substitution normally occurs progressively on different metal centres. For example, in the compound $Os_3(CO)_9(PR_3)_3$, an equatorial carbonyl group has been replaced on each metal centre.[17] These substitution reactions are very sensitive to the reaction conditions and many of the compounds may react further to form mixed derivatives, or undergo fragmentation of the ligand while maintaining the cluster identity. Nyholm reported that the reaction of $Os_3(CO)_{12}$ with PPh_3 yielded no less than nine products.[18] Three of these were identified as substituted compounds of the type $Os_3(CO)_{12-x}(Ph_3P)_x$(x=1,2 or 3), while the other displayed evidence of C-H or P-C bond cleavage.

The preparation of substituted clusters such as $Os_3(CO)_{10}(C_6H_8)$ and $Os_3(CO)_{10}(C_8H_{14})_2$ can be achieved in high yields. These compounds have been utilised as useful precursors; they allow the number of products obtained in a reaction to be controlled. The cyclohexadiene complex was initially prepared from the reaction of $H_2Os_3(CO)_{10}$ with 1,3- or 1,4-cyclohexadiene.[19] The compound is stable and readily reacts with a range of ligands to yield disubstituted compounds as shown in Figure 1.1

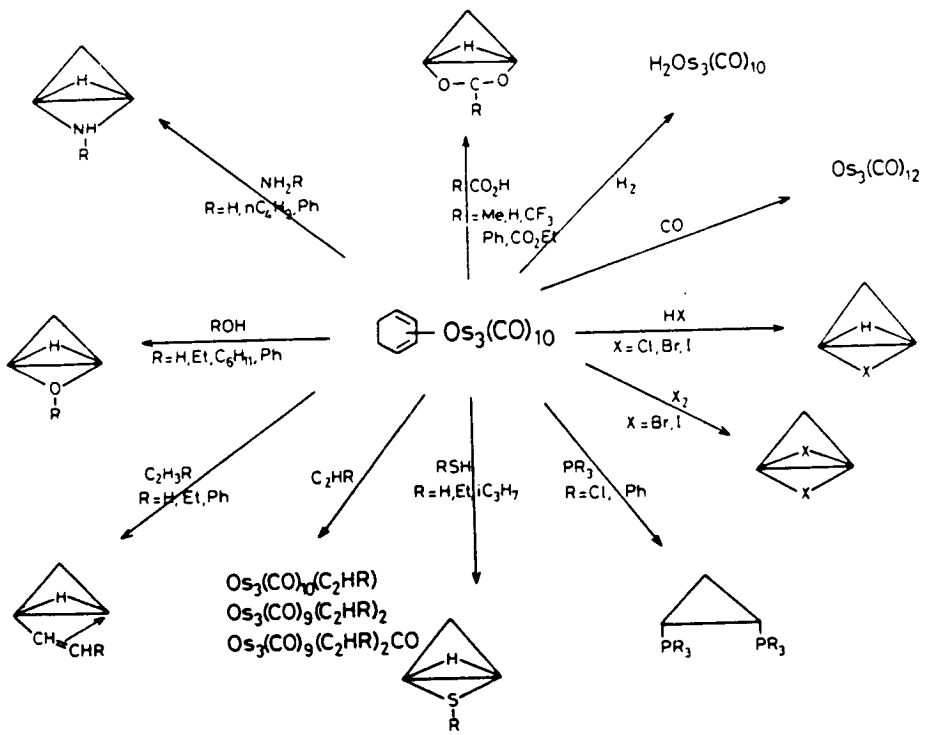


Figure 1.1: Reactions of $Os_3(CO)_{10}(C_6H_8)$

These displacement reactions provide a facile route to a wide range of new compounds, in high yields. It should be noted that most of the compounds formed involve the formation of a hydrido species, this is due to an initial attack on the diene to produce a π-allylic intermediate. The cyclooctene triosmium complex was first isolated from the reaction of cyclooctene with $H_2Os_3(CO)_{10}$ in the presence of ethylene.[20] The ^{13}C nmr spectrum indicates that substitution has occurred at the equatorial sites on two different metal centres. This compound again readily reacts with a range of reagents forming disubstituted compounds inaccessible by other routes.

The approach to substitution chemistry of triosmium clusters most employed today, involves the mono- and disubstituted acetonitrile compounds $Os_3(CO)_{12-n}(MeCN)_n$ (n=1,2).[21] These compounds can be prepared from the reaction of $Os_3(CO)_{12}$ with trimethylamine N-oxide in the presence of acetonitrile. The use of amine oxides (R_3NO) to remove co-ordinated carbon monoxide was first reported by Shvo and Hazum.[22] The carbon monoxide is removed as carbon dioxide, the mechanism is considered to involve the nucleophilic addition of the amine oxide to the co-ordinated CO ligand. This synthetic approach has provided a way to control substitution chemistry in clusters. The MeCN ligand is highly labile and can be easily displaced by a range of other donor ligands, under mild conditions. In many instances it may not be necessary to isolate the acetonitrile derivative or even carry out the reaction in the presence of acetonitrile. This method of chemical activation is used extensively throughout cluster chemistry. [23-25]

1.1.4 Addition reactions

The compound $H_2Os_3(CO)_{10}$, provides an alternative route to many substituted triosmium clusters. This useful starting material can be easily prepared by the reaction of H_2 gas with $Os_3(CO)_{12}$.[26] The structure of $H_2Os_3(CO)_{10}$ provides an example of an "unsaturated" 46 electron cluster system. The 18 electron rule suggests that this compound has an Os-Os double bond, which appears to be supported by the reduced bond length of 2.68Å as opposed to 2.82Å for a normal Os-Os bond. However, it is unlikely that there is a build up of electron density along the Os-Os direction, but rather metal-metal interactions are likely to take place through the bridging atoms. It is of interest to compare $H_2Os_3(CO)_{10}$ with the bridging in B_2H_6.[27] The OsH_2Os group involves four centre four electron bonding, employing d^2sp^3 hybrid metal orbitals as shown in Figure 1.2.

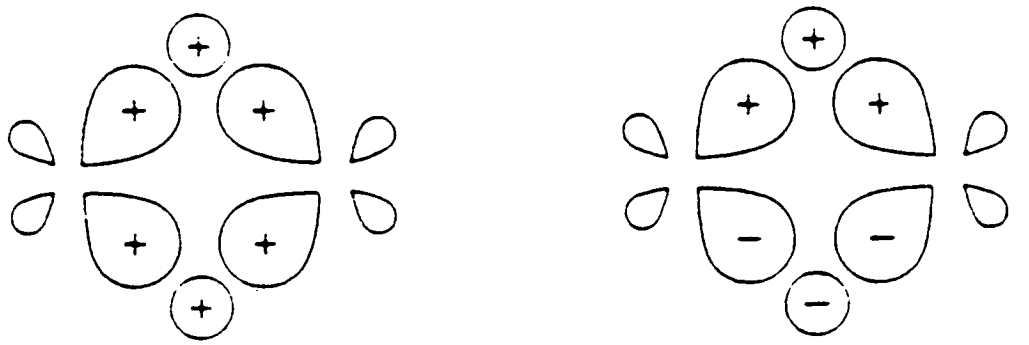


Figure 1.2: Occupied bonding orbitals in the dihydride bridges of $H_2Os_3(CO)_{10}$

Whatever, the electronic structure of $H_2Os_3(CO)_{10}$, the reaction with donor molecules certainly implies unsaturation. If CO gas is bubbled through a solution of $H_2Os_3(CO)_{10}$, the compound $H_2Os_3(CO)_{11}$ is formed.[28] The addition products of the type $H_2Os_3(CO)_{10}L$ (L=PR_3,CNR, C_5H_5N) involve a bridging hydride and a terminal hydride. Nmr studies have demonstrated that phosphorus ligands occupy equatorial sites, whereas, pyridines and isonitriles bond in axial positions. The major drawback of using $H_2Os_3(CO)_{10}$ as a starting material, involves the hydrogenation of products, a problem that does not arise in the previously considered displacement reactions.

1.2 Arene sandwich complexes

The interactions between arenes and metal complexes has played an important role in the development of organometallic chemistry. The first arene-metal complexes were identified by Hein in 1919[29], who isolated his "phenyl-chromium compounds" from the reaction of $CrCl_3$ and PhMgBr. Although, they were not identified until much later by Zeiss as (η^6-benzene)(η^6-arene) chromium (I) complex cations [arene= benzene, biphenyl].[30] The classic studies by Fischer in the mid-1950's, using the reducing "Friedel-Crafts method", found a rational synthesis for *bis* (η^6-benzene) chromium and with it laid the foundations for a rapidly expanding chemistry.[31]

The 18 electron, diamagnetic Cr(0) complexes $Cr(\eta^6\text{-}C_6H_6)_2$ and $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ are classic examples of sandwich and half sandwich systems containing planar benzene ligands.[31] Electron diffraction and low temperature X-ray crystallographic studies of $Cr(\eta^6\text{-}C_6H_6)_2$ have established an eclipsed, D_{6h} geometry in both the gas phase[32] and the solid state.[33]

A generalised molecular orbital diagram for *bis* (benzene) metal complexes of D_{6h} symmetry is shown in Figure 1.3.[34] A shorthand representation has been used for the in-phase and out-phase combinations of π-orbitals, that emphasise their nodal characteristics. The a_{1g}, a_{2u} and e_{1u} benzene π-sets are stabilised by the metal s and p orbitals. The benzene molecular e_{1g} orbital is also stabilised by the chromium xz and yz orbitals. Therefore, there are a total of six strong bonding interactions between the chromium and the two benzene molecules. The molecular orbitals $2a_{1g}$ and $1e_{2g}$ are essentially non-bonding. Six electrons will be housed in these levels plus twelve electrons in the six bonding levels to give the eighteen electrons previously mentioned.

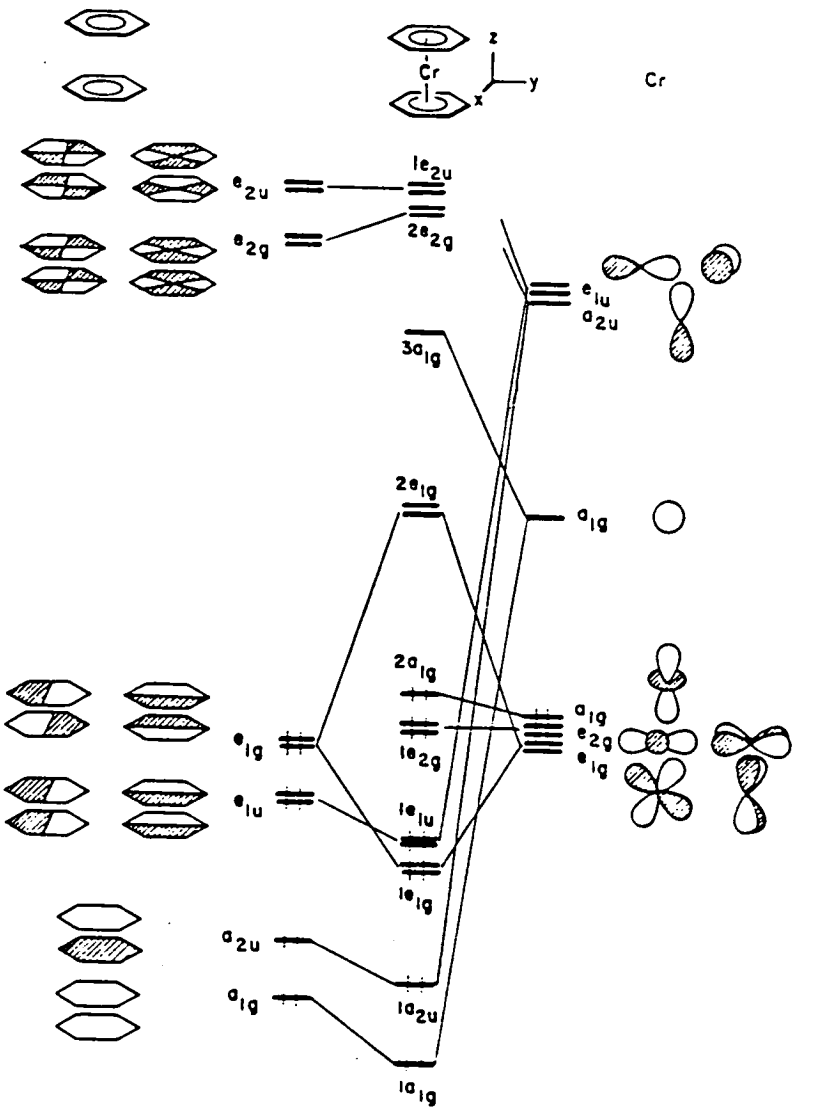


Figure 1.3: The generalised molecular orbital diagram for *bis* (benzene) chromium

The bonding for *bis* (benzene) chromium described above was based on a delocalised molecular orbital framework. However, a localised valence bond model could have been constructed as six equivalent d^2sp^3 hybrid orbitals. [35] The hybrid bonds point towards the vertices of an octahedron and the six π-bonds of the benzene molecules match them perfectly in a spatial sense. This leaves three atomic orbitals (d_z2, $d_x2\text{-}y2$, d_{xy}) unused in the hybridisation and they are therefore non-bonding.

The prototypical $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ has been structurally analysed at low temperatures by both X-ray[36] and neutron diffraction techniques.[37] Studies indicate the staggered confirmation is preferred to the eclipsed orientation. The three ring C-C bonds that are eclipsed by the carbonyl groups are significantly longer than the non-eclipsed C-C bonds (1.423 vs 1.406Å), representing a reduction in symmetry for the benzene ligand from D_{6h} to C_{3v}. The ring hydrogen atoms are displaced on average 0.03Å from the benzene plane towards the chromium atom, this may be explained in terms of reorientation of the benzene molecular orbitals for a more efficient overlap with the metal based orbitals.[38]

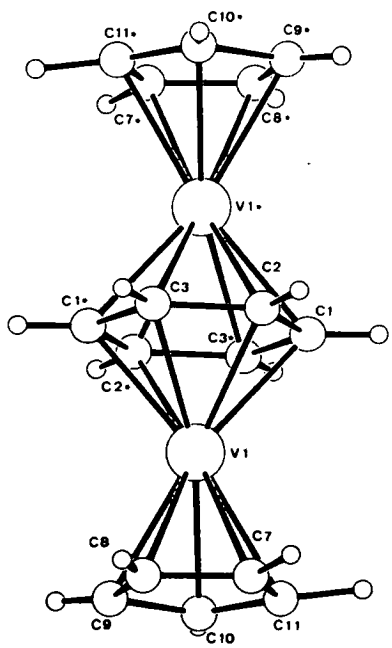


Figure 1.4: The molecular structure of the triple-decker sandwich $(CpV)_2(\mu\text{-}\eta^6\text{-}C_6H_6)$

The first example of a triple-decker sandwich complex containing a bridging benzene was reported by Krüger in 1983.[39] Until then, triple and tetra-decker sandwich complexes had only been prepared with five or eight membered carbocyclic or heterocyclic groups.[40-42] The molecular structure of $(CpV)_2(\mu\text{-}\eta^6\text{-}C_6H_6)$ is depicted in

Figure 1.4. In this complex two cyclopentadienyl vanadium moieties are linked by a bridging benzene. The compound can be prepared by the reaction of $CpV(C_3H_5)_2$ with an excess of 1,3 cyclohexadiene in refluxing n-heptane. It is interesting to note that the complex can undergo arene exchange reactions with the retention of the triple-decker sandwich structure to form toluene and mesitylene analogues.

In 1986, the first triple-decker sandwich containing bridging and terminal arene ligands was reported.[43] The reaction of chromium vapour with mesitylene at high metal to ligand ratios led to the formation of an unusual dinuclear complex, which was initially formulated on the basis of variable temperature ^1H and ^{13}C nmr as the novel triple-decker sandwich $(\eta^6\text{-}C_6Me_3H_3)_2(\mu\text{:}\eta^6\text{:}\eta^6\text{-}C_6H_6)Cr_2$. The structure was later confirmed by X-ray crystal analysis.[44] The structure shows all three mesitylene rings are planar, parallel and nearly eclipsed.

1.3 Arene cluster chemistry

1.3.1 Introduction

While the chemistry of mononuclear arene-metal complexes has been exhaustively reported[45-47], the study of the interaction between arenes and metal clusters continues to flourish and has been the subject of a recent review article by Johnson *et al* .[48] A number of synthetic routes are available for the production of arene clusters, in general they can be classified into two types. The first, where the arene ligand is added directly, in this case activation of the cluster is by thermal or photolytic means and often results in a change of cluster nuclearity. A more selective approach involves the chemical activation of the cluster and addition of the appropriate 1,3- or 1,4-cyclohexadiene ligands. These can be converted to the corresponding arene complexes at a later stage.

1.3.2 η^6-co-ordination in clusters

The most commonly observed co-ordination for arene ligands in cluster chemistry is the η^6-mode, where the organic moiety is terminally bound to one metal atom donating all six electrons. Hexaruthenium complexes containing η^6-arenes were amongst the earliest examples of arene clusters. The original preparation of these compounds involved the thermolysis of $Ru_3(CO)_{12}$ with the appropriate arene,[49] although yields were relatively small. Two alternative methods for the preparation of the compound $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ have been found. A high yielding reaction involving the ionic coupling between the pentanuclear dianionic cluster $[Ru_5C(CO)_{14}]^{2-}$ and the cationic

benzene fragment $[Ru(\eta^6\text{-}C_6H_6)(PhCN)_3]^{2+}$ affords the hexa ruthenium benzene cluster.[50]

Alternatively, the hexaruthenium benzene complex may be prepared by the activation of the parent cluster $Ru_6C(CO)_{17}$ with trimethylamine N-oxide in a solution containing the cyclohexadiene ligand. Both the diene and the benzene complexes $Ru_6C(CO)_{15}(\mu_2{:}\eta^2{:}\eta^2\text{-}C_6H_8)$ and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ are observed . The diene complex can be easily converted to the benzene complex by the addition of Me_3NO. Similar reactions have been observed for the pentaruthenium cluster $Ru_5C(CO)_{15}$[51,52]and the tetraosmium cluster $H_4Os_4(CO)_{12}$.[53] Several tri- and tetranuclear cobalt clusters containing η^6-arene ligands are also known. A feature common to all tricobalt arene clusters is the presence of a triply bridging ligand such as MeC, PhC or CO. This ligand caps one side of the metal triangle. Monoarene complexes of the type $RCCo_3(CO)_6(\eta^6\text{-arene})$ (R=Ph, arene= C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$) can be prepared in good yields from the direct reaction of $RCCo_3(CO)_9$ with the appropriate arene.[54] Similarly, tetracobalt arene clusters are easily prepared by a straightforward thermolysis of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ in an arene solvent.[55]

1.3.3 The face-capping mode

In 1985, the synthesis of compounds $Ru_6C(CO)_{11}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ and $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ was reported. These complexes demonstrated the first examples of a facially bound arene ligand.[56] The synthesis of both compounds is depicted in Figure 1.5. The hexaruthenium cluster was isolated as the major product from the reaction of the dianionic cluster $[Ru_6C(CO)_{13}(\eta^6\text{-}C_6H_6)]^{2-}$ with the cationic capping fragment $[Ru(\eta^6\text{-}C_6H_6)(PhCN)_3]^{2+}$. A heptanuclear cluster would be expected from this reaction. However, the octahedral metal framework remains intact with the introduction of a second benzene moiety to the cluster.

The preparation of the triosmium complex involves the stepwise "dehydrogenation" of the triply bridging cyclohexadienyl complex $HOs_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_6H_7)$, this compound was initially prepared from the reaction of $H_2Os_3(CO)_{10}$ with 1,3 cyclohexadiene in 1977.[19] A hydride can be abstracted from the dienyl ring using triphenylmethyl(trityl) cation, generating the cationic hydrido benzene species $[HOs_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]^+$, which can be readily deprotonated at the metal triangle by the non-nucleophilic base DBU as shown in Figure 1.5.

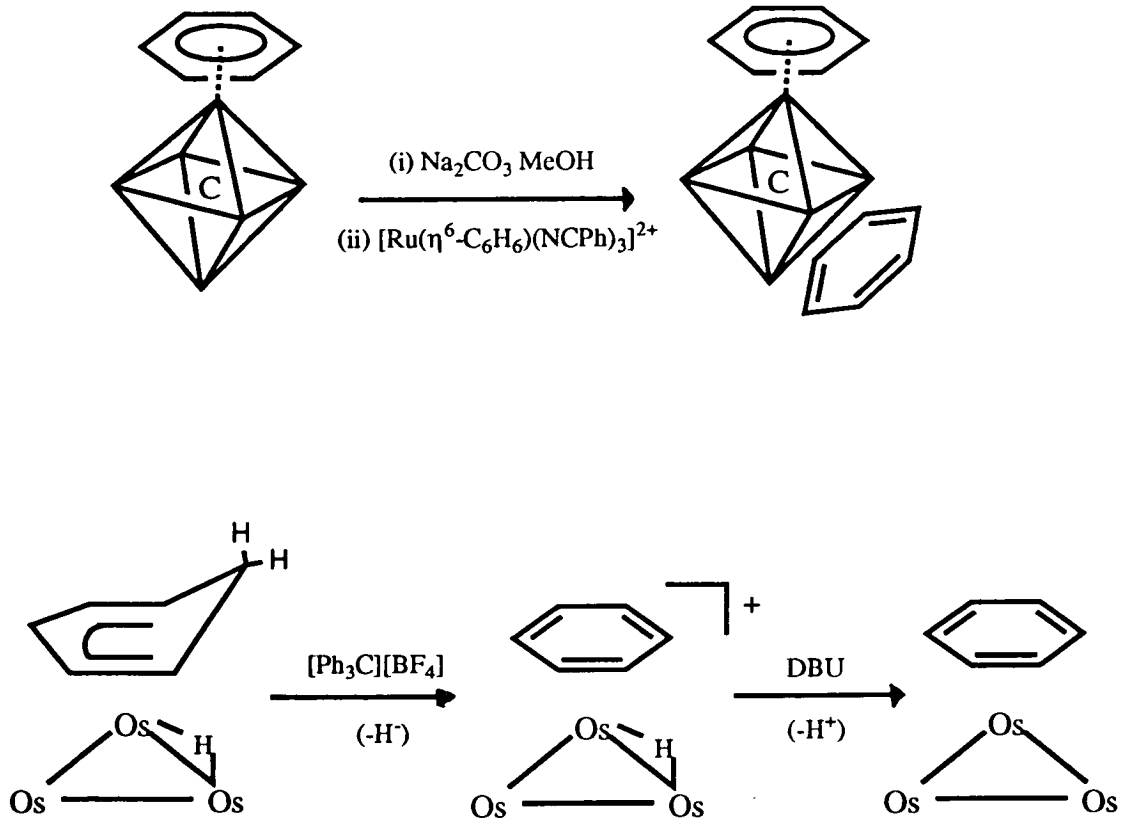


Figure 1.5: Synthesis of face capping benzene compounds.

Both compounds have been characterised crystallographically and the molecular structures are shown in Figure 1.6. The structure of the hexaruthenium *bis* -benzene compound is derived from the parent hexaruthenium carbido cluster $Ru_6C(CO)_{17}$.[57] Substitution of three terminally bound CO groups on an apical ruthenium atom for an η^6-benzene molecule demonstrates the conventional co-ordination mode for benzene. However, the replacement of three carbonyl ligands at a triangular face allows the second benzene moiety to demonstrate the new μ_3:η^2:η^2:η^2-co-ordination. An interesting feature of this facial benzene ligand is the alternating 'long-short-long' bond pattern, where the mean co-ordinated C-C distances are 1.39Å as opposed to 1.48Å for those non-co-ordinated distances. This apparent bond localisation leads to the adoption of a Kekulé type structure, where the distortion of the ring tends towards a hypothetical cyclohexatriene molecule. This aspect shall be addressed in greater detail in section 1.5.

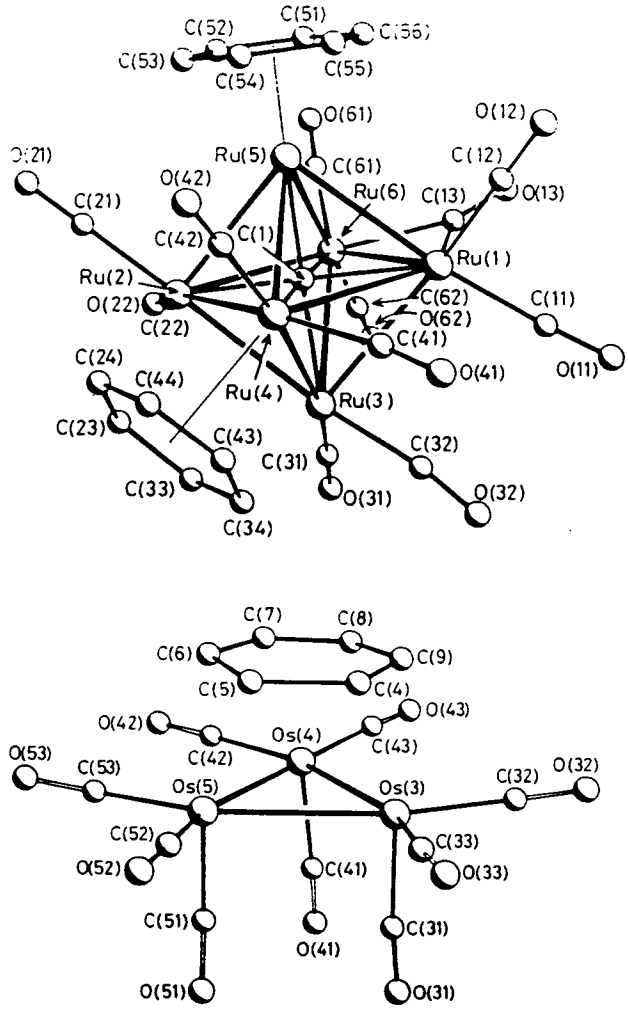


Figure 1.6: The molecular structures of $Ru_6C(CO)_{11}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ and $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$

The triosmium cluster has approximate C_{3v} symmetry, the benzene ring is almost parallel to the Os_3 triangle, an axial carbonyl group has been replaced on each metal atom. Again. a Kekulé distortion of the benzene ring can be seen, but high estimated standard deviations render this observation insignificant.

The face capping co-ordination of arenes has been reported for the tricobalt cluster $Co_3Cp_3(\mu_3\text{-arene})$.[58] The synthesis of this compound is unusual in that the cluster assembles itself on the arene and involves a step-like reaction between $CpCo(C_2H_4)_2$ and substituted styrenes. Due to the simple fact that simple arenes do not undergo this reaction, it would appear that the initial binding of the metal fragment is at the alkenyl group before attack at the aromatic π-system occurs. The second and third cobalt units must then attack in a *syn* position. The postulated mechanism for the preparation of $Co_3Cp_3(\mu_3\text{-arene})$ is demonstrated in Figure 1.7. The rhodium analogue $[RhCp]_3(\mu_3$-

C_6H_6) can be obtained by the successive co-ordination of RhCp fragments to benzene in a hexane solution, where the RhCp fragments have been generated by the photolysis of the stable complex $CpRh(C_2H_4)_2$.[59]

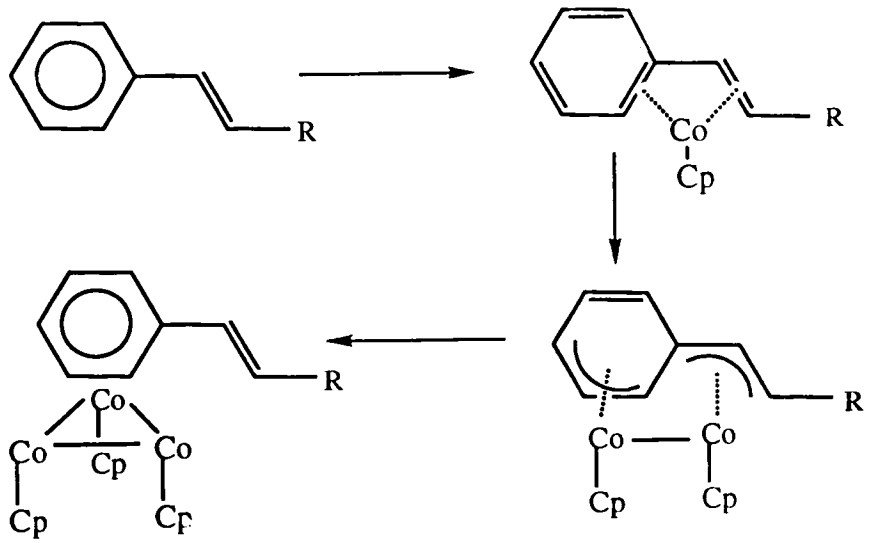


Figure 1.7: The proposed formation of $Co_3Cp_3(\mu_3\text{-arene})$ from $CpCo(C_2H_4)_2$

1.4 Cluster-surface analogy

1.4.1 Introduction

The analogy between molecular metal clusters and metal surfaces has been the subject of serious debate over the years. Heterogeneous catalysis forms the basis of many industrially important chemical processes, yet the understanding of the associated surface chemistry is poorly developed at the molecular level.[60] Physical techniques such as X-ray crystallography and nmr spectroscopy, used routinely by molecular chemists are not generally applicable for structural characterisation of the chemisorbed states of a molecule on a surface. Low-energy electron diffraction (LEED), High-resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES) are valuable techniques employed by surface scientists. However, these methods do not offer the precision available in molecular structural analysis. Whatever the limitations of the proposed analogy, it is worth emphasising that comparisons between the vibrational spectra of molecular metal clusters (characterised by crystallography) with spectra obtained from adsorbed species are crucial to surface scientists, in order to determine the structures of adsorbates on metal surfaces.[61]

A detailed assessment of the metal cluster analogy has been reported by Muetterties, concentrating mainly on the chemisorption process.[61] From his observations, it would appear the critical elements that must be considered in the assessment of the validity of the analogy are size, co-ordination number, structure and stereochemistry, thermodynamics and ligand mobility. Each of these will be discussed in turn.

1.4.2 Size

To the inorganic chemist molecular clusters are large in size, however, even the largest of these is only a sub-microscopic fragment of a metal surface. The most commonly studied clusters contain three, four or six metal atoms. Can these smaller clusters therefore be feasible models of a surface.

For a cluster to truly possess the properties of a metal, hundreds of metal atoms would be required. Calculations based on σ-molecular orbital theory and extended Hückel calculations indicate that a hypothetical cluster ranging from 25-50 atoms (depending on the metal) would be metal-like in character.[62,63] Small 4-6 atom clusters are therefore not metal-like. However, the cluster-surface model is not structured on this comparison but on the comparison between a discrete metal cluster with a polyhedral metal core and a periphery of ligands and a metal surface with a similar set of chemisorbed ligands.[61] A 'surface-molecule' concept has been employed which assumes adsorbed molecules interact strongly with a limited set of metal atoms on a surface. It appears that a minimum of three-four atoms are needed to describe the 'cluster-like' surface chemical bond.[64]

1.4.3 Co-ordination number

Metal clusters are largely deltahedra, polyhedra with all triangular faces. The metal framework of most clusters represents fragments of close-packed arrays. However, a few distinctive examples exists, $Rh_{13}(CO)_{24}H_3^{2-}$,[65] and $Rh_{13}(CO)_{25}^{4-}$,[66] which can be considered as fragments of hexagonal close packed and body centred cubic structures.

Metal atom co-ordination is uniformly higher for atoms in surfaces than for atoms in clusters. The atoms in a close packed array on a surface have a co-ordination number of nine, this may fall to seven or six for surfaces with high miller index planes, where a small number of surface sites (steps and kinks) may be found. The co-ordination numbers of metal atoms in clusters are relatively low, two in triangular systems, three in tetrahedra, four in octahedra up to a maximum of seven in some larger polyhedra. For metal-ligand interactions the inverse holds true. The metal atom connectivity in clusters

is large, three to five, whereas for a metal surface, the average is less than one. Only in the cluster $Pt_{19}(CO)_{12}^{4-}$ does the metal-ligand connectivity drop below one.[67] These variances for the two cases represents a breakdown in the analogy for smaller clusters (3-12) but not for some of the larger clusters $Rh_{15}(CO)_{27}^{3-}$ and $Pt_{19}(CO)_{12}^{4-}$. Therefore, a flat or nearly flat surface cannot be modelled by a polyhedral metal cluster. The significance of these differences becomes less critical when structural and thermochemical variances are discussed.

1.4.4 Structure and stereochemistry

In order to make structural comparisons between the chemisorbed state and metal clusters, there must be optimal correspondence in the metal, ligand type, ligand coverage and crystallography.[61] The first three constraints pose no tactical problems. Although, it may be unrealistic to prepare cluster compounds containing only one ligand type e.g. ethylene or hydrogen, synthesis of such clusters in combination with other ligands e.g. carbon monoxide are well documented and easily obtained. Most clusters are co-ordinatively saturated, analogy is achieved by metal surfaces with monolayer coverage. The major discrepancy occurs when considering crystallography. Structurally, molecular clusters are polyhedra with triangular faces, this makes them poor models for flat surfaces. Improved comparison is achieved for high Miller index planes, where not only is the surface atom co-ordination number lower than for low Miller index planes, but irregular features such as steps and kinks can also develop. Correspondence in the two regimes increases as the chemisorbed metal surface is changed from a single crystal to a film or small particles. Unfortunately, as the surface becomes more complicated the number of applicable surface techniques decreases.

In general many ligands, conventionally unidentate in mononuclear complexes, exhibit multicentre metal atom interactions in clusters. If the structure, stereochemistry and bonding of simplistic ligands are so dramatically altered in going from mononuclear chemistry to clusters, then it is feasible to expect a complex and typically multicentred interaction on a clean metal surface. Indeed studies have established multicentre metal absorbate interactions and therefore the metal-surface analogy appears to be valid. Several organic molecules and molecular fragments that have been identified on a metal surface are depicted in Figure 1.8. These species have the same local structure and similar chemistry to those found in multinuclear organometallic clusters for which there is good X-ray diffraction information available.[64] For virtually every organic surface species found so far, there is a cluster equivalent that has been

synthesised by organometallic chemists.[68] The comparison for benzene and other arenes will be discussed shortly.

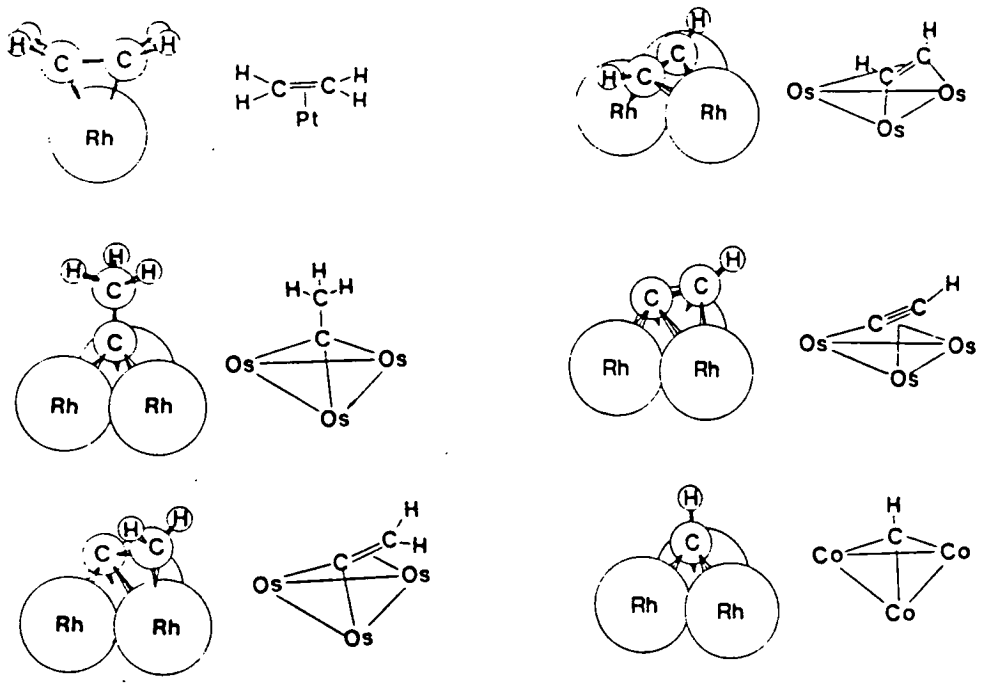


Figure 1.8: Cluster-like adsorbed species on rhodium metal surfaces

1.4.5 Thermochemistry

The comparison of heterogeneous surface chemistry of metal clusters and of chemisorption on extended surfaces can in principle provide insights into the nature of chemical bonding. However, thermochemical data for metal-metal interactions in metal clusters and metal surfaces are not easily accessible. Although the calorimetric data for metal-metal bond energies in clusters and surfaces are frequently close, no accurate quantitative comparison can be made.[61,69] This is due to large assumptions such as the surface metal-metal bond energies being comparable to those derived in bulk metal. Metal-ligand bond energies can be determined more reliably especially for surfaces where adsorption-desorption equilibria are readily probed. For carbon monoxide ligands, energy values tend to be 30-50% smaller in clusters than for the chemisorbed state.[70] However, values can increase as the crystallography changes from low densely

packed Miller index planes to higher more open planes(i.e. as the metal connectivity approaches that of a cluster).[71]

1.4.6 Ligand mobility

Spectroscopic, calorimetric and kinetic studies of metal clusters and chemisorbed metal surfaces have demonstrated that in some instances the ligands are mobile.[61,69] This mobility may arise from two fundamental mechanisms. Firstly, a dissociative process in which all bonds between the ligand and cluster or metal surface are broken. The ligand would appear as a discrete entity in solution in the cluster case, or in the solution or gas phase for the metal surface. The alternative process involves a non-dissociative migration of the ligand about the periphery of the cluster or surface. This non-dissociative mechanism can have substantially lower activation energy than the alternative dissociative process. With respect to catalysis migration of organic ligands is of extreme importance in both clusters and surfaces.

Nmr spectroscopic techniques are an invaluable tool for the detection of ligand migration or fluxionality in cluster complexes. In surface science the major technique employed is Field Emission Microscopy, although an initial indication of ligand mobility may be obtained from differential heats of diffusion or kinetic studies.

Molecular clusters are co-ordinatively saturated, in order for a direct analogy for ligand mobility in the two systems to be realised the surface must have monolayer coverage. For clusters, localised ligand migration between two metal atoms in the cluster is unfavourable, a concerted motion of the ligand set is required for migration to occur. On a metal surface with less than monolayer coverage ligand motion is localised and non-concerted, only at monolayer coverage when the ligand migration rate decreases and concerted movement of the ligands is required for ligand mobility does the surface become comparable with the cluster.

Mechanistic information for many low energy ligand processes on clusters is readily available. Unfortunately, these processes involve a ligand set that is almost coplanar with the metal face, this cannot be emulated on flat close packed surfaces. It may be possible for tiny metal particles or irregular surfaces where the spacial freedom above the surface is restricted. In catalysis the metal surface is uneven therefore the analogy may become valid.

To reiterate the analogy between metal clusters and chemisorbed states on metal surfaces is subject to many boundary conditions. The major breakdown occurs in the crystallographic differences of the two systems. Flat close-packed surfaces have no structural analogues in the discrete metal clusters and therefore, comparison is at best strained. However, structural features of the chemisorbed states of molecules have been shown to be similar to those of the same molecule bound in a metal cluster. As the surface develops irregularities at high Miller index planes, the analogy becomes more valid. A catalytic metal surface is rough and uneven, possibly as surface techniques improve the validity of comparing clusters to surfaces may be realised.

1.5 Molecular models for benzene chemisorption on metal surfaces

Advances in the dynamical theory of low-energy electron diffraction (LEED) by ordered adsorbate overlayers has led to the structural characterisation of several surface-metal benzene complexes by Somarjai, Van Hove and others.[73] Benzene is primarily bound in a π-fashion with the C_6-ring remaining intact, nearly parallel to the surface plane. Various adsorption sites have been reported and are depicted in Figure 1.9[72]

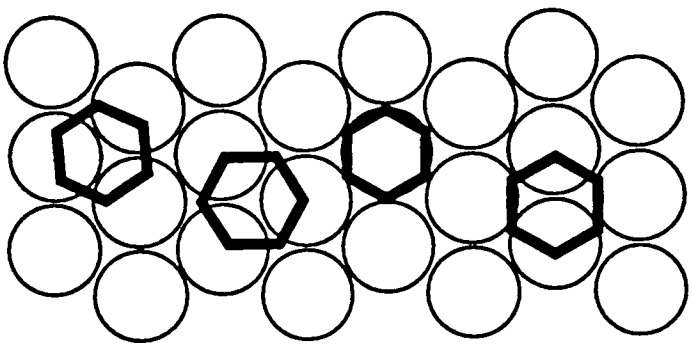


Figure 1.9: Modes of benzene chemisorption

The benzene molecule can occupy three different symmetry sites. These being the so called "hollow" ($C_{3v\sigma d}$, σv), "on-top" (C_{6v}) and "bridging sites" (C_{2v}). In order to perform studies of adsorbed benzene on Pd(111)[73], Rh(111)[74] and Pt(111)[75] metal surfaces, it is necessary to coadsorb carbon monoxide to induce an ordered structure on the surface. This ordering may be explained in terms of electron acceptor-donor interactions between the benzene and the CO molecules, no evidence for covalent bonding between the two exists.

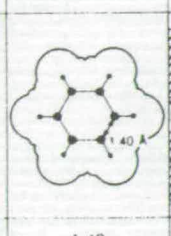
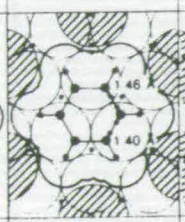
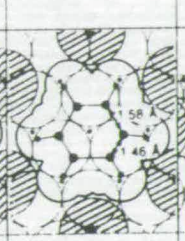
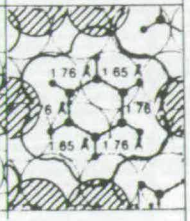
Substrate	(Gas Phase)	Pd(111)	Rh(111)		Pt(111)
Surface Structure		(3x3)-C_6H_6 + 2CO	(3x3)-C_6H_6 + 2CO	c(2√3x4)rect-C_6H_6 + CO	(2√3x4)rect-$2C_6H_6$ +4CO
The Structure of Benzene					
C_6 Ring Radius (Å)	1.40	1.43±0.10	1.51±0.15	1.65±0.15	1.72±0.15
d_{M-C}(Å)	-	2.39±0.05	2.30±0.05	2.35±0.05	2.25±0.05
γ_{CH}(cm^{-1})*	670	720-770	780-810		830-850

Figure 1.10: Benzene chemisorption on metal surfaces

LEED analysis has shown that bonding within the adsorbed benzene molecule varies from one ordered structure to another, Figure 1.10. In all cases the benzene ring expands as indicated by the increase of the ring radii. For Pt(111), the benzene molecule occupies a "bridging" site, whereas "hollow" sites are observed on the Rh(111) and Pd(111) surfaces, the symmetry of the benzene ring expansion varies with the adsorption site. When the benzene molecule occupies a "hollow" site there appears to be an alternating long-short-long C-C bond pattern in the C_6-ring, resulting in the adoption of a Kekulé-type structure. The effect is most noticeable for the c(2√3x4) rect C_6H_6+CO structure on the Rh(111) surface, the C-C bond distances alternate between a 'long' 1.81Å and a 'shorter' 1.33Å.[76] The short bonds lie above single metal atoms, whereas the long C-C bonds form bridges linking pairs of metal atoms. The benzene resembles three acetylene molecules; however, the expected Van der Waal's separation between two acetylenes is approximately 2.8Å. Therefore, the adsorbate is still considered a distorted benzene molecule.

In 1985, the synthesis of the compounds $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ and $Os_3(CO)_9(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ was reported by Wright and co-workers.[56] These complexes contain a benzene moiety bound to a *triangulo* cluster face and bear a striking resemblance to benzene chemisorbed on single Rh(111)[76] and Os(001)[77] surfaces. The benzene ligands show trigonal distortions towards a hypothetical

cyclohexa-1,3,5-triene with bond lengths ranging from 'long' 1.48Å and 'short' 1.39Å, Figure 1.11

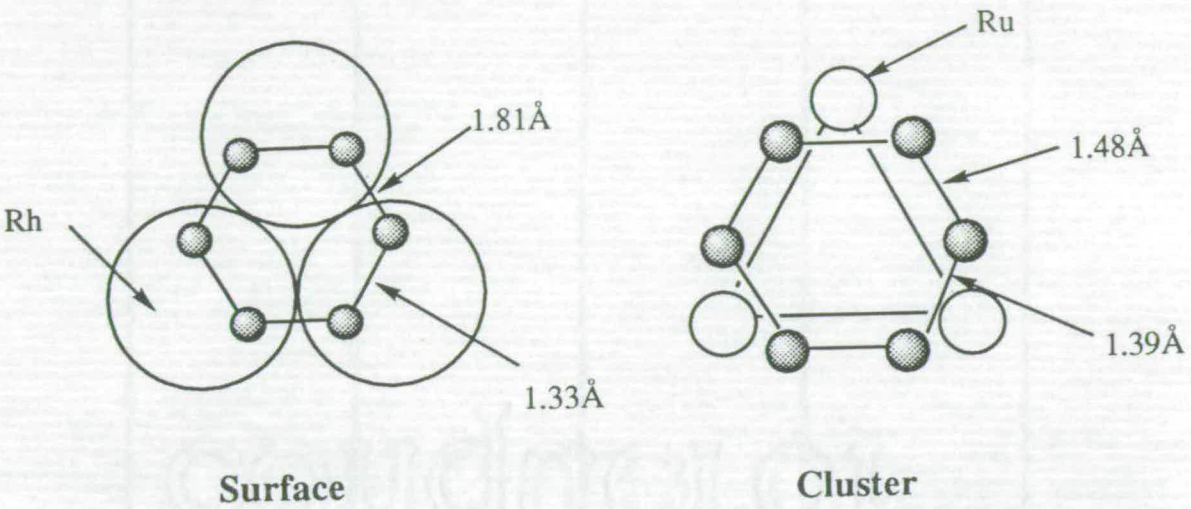


Figure 1.11: Benzene distortion on a Rh(111) metal surface and on a ruthenium cluster.

The difference between the 'long' and the 'short' C-C bonds of the benzene ring in trinuclear clusters [$M_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ M=Ru,[78] Os[56]] is 0.04Å and 0.10Å respectively. This difference increases to 0.08Å in the pentaruthenium cluster $Ru_5C(CO)_{12}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and 0.09Å in hexaruthenium clusters. It would appear that the distortion in the ring becomes more pronounced as the nuclearity of the cluster increases. For the Rh(111) surface the difference between bond lengths is approximately 0.5Å, although the high estimated standard deviations render this less significant, a single metal surface could be thought of as a giant cluster. Both the metal and the cluster systems display out of plane C-H bond bending away from the metal. This may be explained in terms of rehybridisation from sp^2 towards sp^3, allowing maximum overlap of the π-system with the metal orbitals.[38]

Thermal desorption and molecular displacement reactions of benzene have been studied on flat and stepped Pt surfaces.[79,80] On a flat Pt(111) surface, chemisorbed benzene can be partially displaced (90%) by trimethylphosphine. For a monolayer coverage of less than 0.1, the benzene molecules appear to be irreversibly bound.

However, as monolayer coverage increases, thermal desorption behaviour consistent with two different chemisorption states of benzene have been observed.

For a stepped Pt 6(111)x(111) surface at less than 0.33 of monolayer coverage, irreversible chemisorption is reported. At higher coverages reversible adsorption clearly indicates two different chemisorption sites; one where the benzene is strongly bound and the other relatively weakly bound. H-D exchange reactions demonstrate that at elevated temperatures, reversible C-H bond cleavage can occur in the more strongly bound state. This effective H-D exchange process is unique to the stepped surface. It appears that the intrinsic topographical features of the stepped surface favour dissociative chemisorption of benzene. The planar co-ordination of the arene parallel to the step allows for the close approach of the C-H hydrogen atoms to the kink or step atoms facilitating C-H bond cleavage, Figure 1.12.

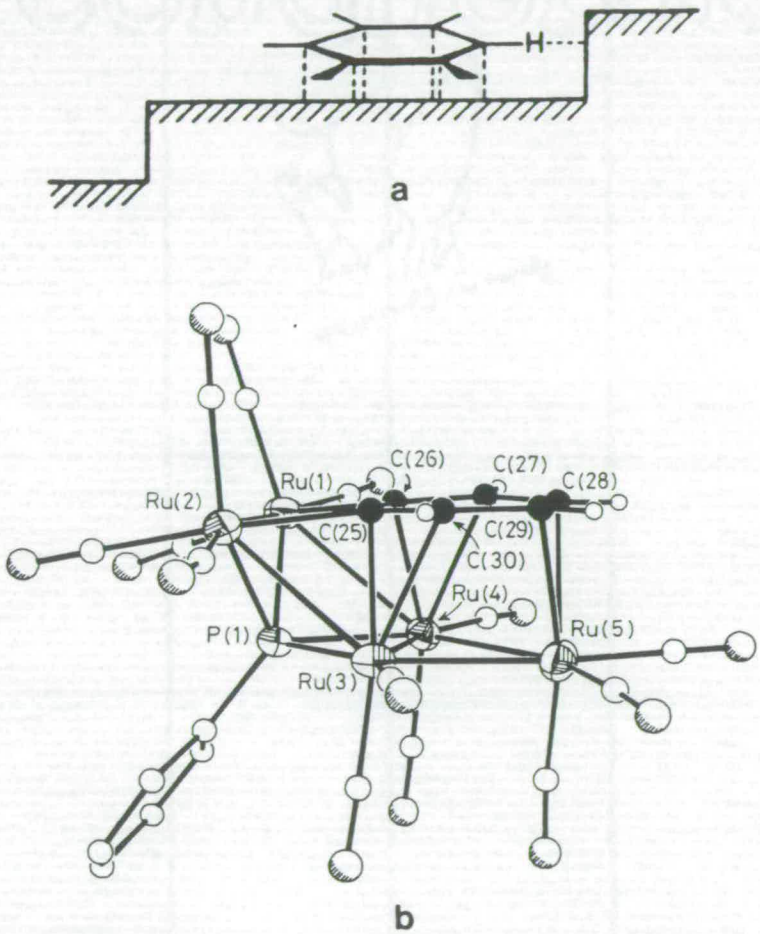


Figure 1.12 a: Representation of a π-bound benzene on a stepped surface, illustrating close approach of C-H hydrogens to step atoms **b:** Molecular structure of $Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_5\text{-}\eta^6\text{-}C_6H_4)$

A cluster model for this process, $Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_5{:}\eta^6\text{-}C_6H_4)$, depicted in Figure 1.12, was proposed by Knox *et al* .[81] The five metal atoms mimic a step-site on a (111) surface, where Ru(3)Ru(4)Ru(5) are in one terrace and Ru(1)Ru(2) are step atoms in the first row of the next. It is envisaged that the approach of benzene to a step on a metal (111) surface will result in the activation of two ortho C-H bonds to generate benzyne chemisorption as shown.

In chapter 3, the photoisomerisation of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ to $H_2Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)$ is described. The postulated mechanism for this process involves the generation of a vacant site at an osmium atom and is thought to mimic the coordinative unsaturation of a metal surface. As has been previously mentioned the $\mu_3{:}\eta^2{:}\eta^2{:}\eta^2$-co-ordination mode for benzene on clusters is thought to accurately model the non-dissociative chemisorption of benzene at a three-fold "hollow" site on the surface of a close packed metal. Therefore, the isomerisation of μ_3 -benzene to μ_3-benzyne in a cluster may be an attractive model for the interconversion of associatively and dissociatively chemisorbed states of benzene on low Miller planes of a metal surface.[82]

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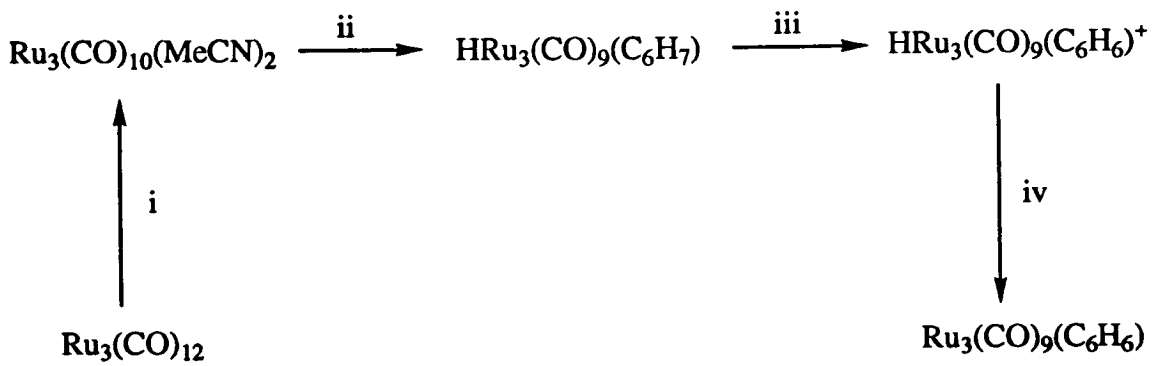
Chapter 2: Diene Cluster complexes

This chapter commences with a brief description of the established synthetic route to the face-capping benzene cluster $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5**. The molecular structure of compound **5**, clearly demonstrates Kekulé-type distortions. An alternative one step synthetic route to $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** has been discovered and is discussed herein. This route has proven to be considerably more convenient than that previously employed. A range of substituted 1,3 cyclohexadiene ligands have been prepared and successfully reacted with $Os_3(CO)_{10}(MeCN)_2$**3**. An attempt to link two triosmium clusters is also reported.

2.1 Introduction

As has been previously mentioned in Section 1.3.3, the face capping co-ordination mode for benzene in carbonyl cluster complexes was first reported in 1985 for the compounds $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4** and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.[1] These molecules are of special interest because they appear to serve as excellent models for the interactions of benzene with a (111) metal surface.[2] The synthetic approach to the triosmium cluster **4** involves the stepwise dehydrogenation of the triply bridging dienyl complex $HOs_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_6H_7)$, which is formed by the reaction of $H_2Os_3(CO)_{12}$ with 1,3- or 1,4-cyclohexadiene.[3] Due to the fact that the corresponding dihydro cluster $H_2Ru_3(CO)_{12}$ is not available, the analogous face-capping triruthenium complex $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** was not reported until 1990.[4] The synthetic approach to the preparation of compound **5** can be seen in Scheme 2.1.



Scheme 2.1: Synthesis of $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** (i) Me_3NO-CH_2Cl_2-MeCN; (ii) 1,3-C_6H_8; (iii) Ph_3CBF_4; (iv) DBU

The activated precursor $Ru_3(CO)_{10}(MeCN)_2$ can be prepared by the reaction of $Ru_3(CO)_{12}$**2** with trimethyl amine N-oxide in the presence of acetonitrile, following the established literature procedure.[5] Reaction of this activated cluster with 1,3 cyclohexadiene in benzene under reflux affords the dienyl cluster $HRu_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_6H_7)$. The stepwise dehydrogenation with trityl tetrafluoroborate and then DBU, parallels the route previously reported in section 1.3.3 for the analogous osmium compound. Yields of compound **5** are moderate and difficulties have been encountered with reliability of steps (ii) and (iv). An alternative route towards $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** will be discussed in Section 2.2.

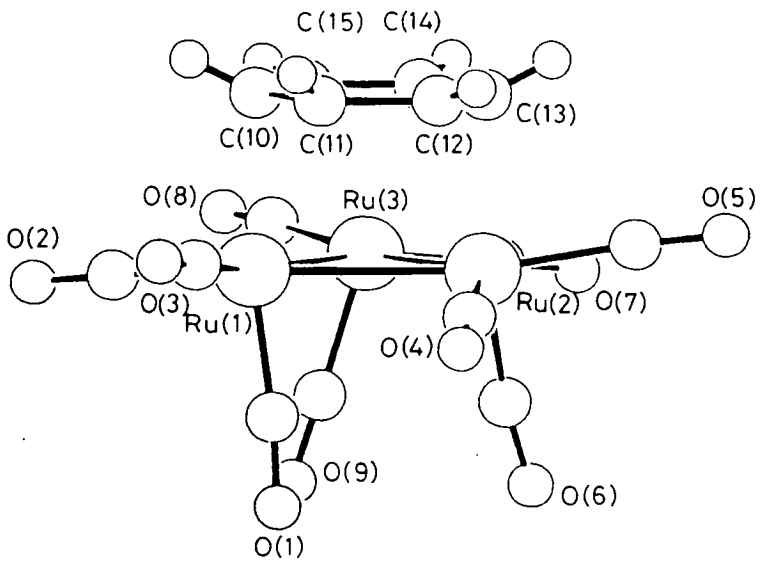


Figure 2.1: The molecular structure of $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5**

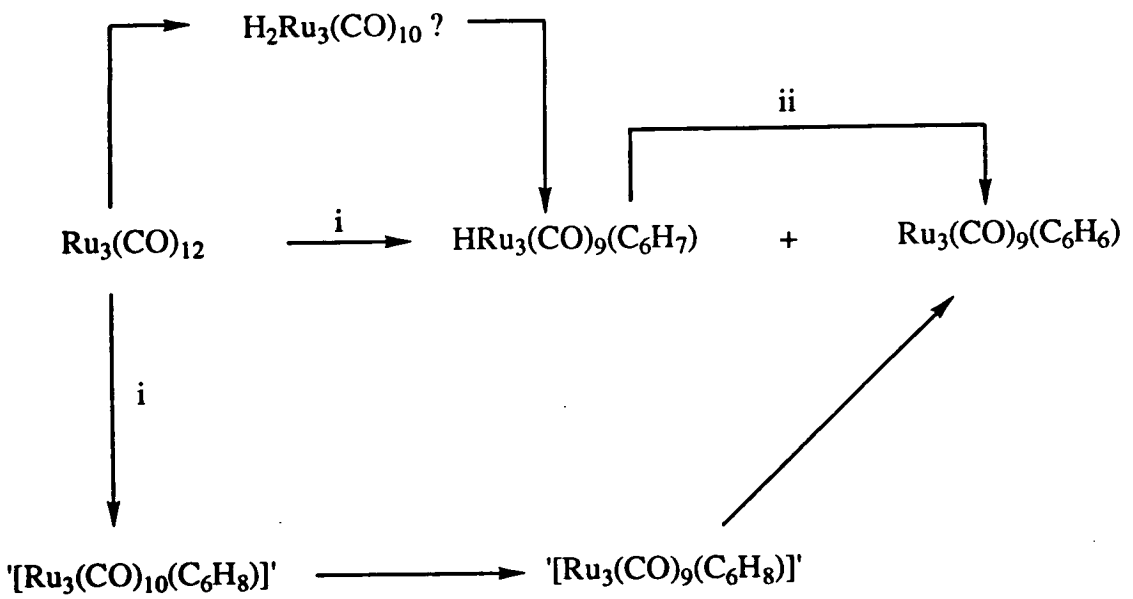
The molecular structure of $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** can be seen in Figure 2.1. It should be emphasised that the data obtained was of excellent quality, allowing the unambiguous description of the bonding between the benzene and the metal frame and direct location of all the H atoms.[6] The metal triangle average bond length of 2.837Å is smaller than that observed in the parent compound $Ru_3(CO)_{12}$**2** of 2.855Å. This shrinkage may be attributed to the less efficient π-accepting capability of benzene with respect to the carbonyl groups. Therefore, there may be a slight increase in bonding electron density over the metal framework. Complex **5** provides clear evidence for a Kekulé-type distortion with 'long' and 'short' C-C bonds [mean 1.45(1) and 1.40(2)Å respectively], alternating within the C_6H_6 ligand. The short bonds being those

interacting directly with the Ru atoms. Kekulé-type distortions have been clearly established previously in the species $(\eta^6\text{-}C_6H_6)Cr(CO)_3$,[7] $(\eta^6\text{-}C_6H_6)Mo(CO)_3$[8] and $(CpCo)_3(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5CH{=}CHMe)$.[9] In Figure 2.1, C-H bond bending away from the metal atoms can clearly be observed (21.1° average with respect to the C_6 plane), resembling the chemisorbed benzene molecule found on the Rh(111) crystal surface.[2]

Continued interest in arene co-ordination to transition metal carbonyl clusters may provide a new insight into the surface chemistry of benzene and other aromatic species, while highlighting possible boundary conditions to any analogy between clusters and surfaces. Optimised synthetic routes to these clusters are therefore required.

2.2 New synthetic routes to $M_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ [M=Ru, Os]

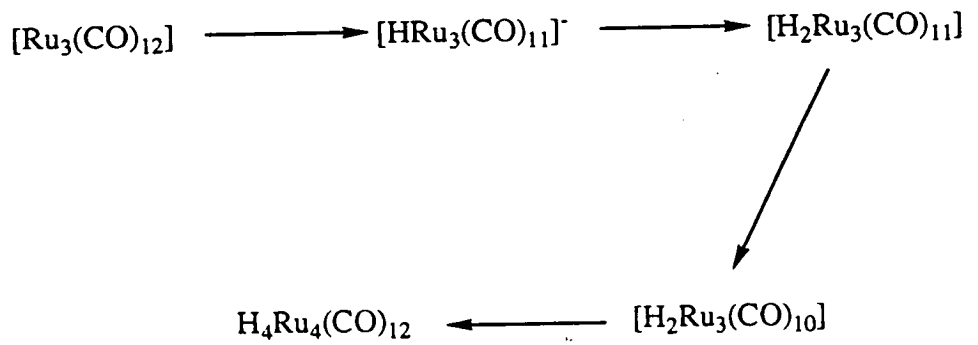
The hexaosmium cluster $Os_6(CO)_{18}$**32** undergoes reaction with trimethyl amine N-oxide to form the highly reactive hydrido species $[HOs_6(CO)_{17}]^-$ and $H_2Os_6(CO)_{17}$.[10] This observation led us to examine the related reactions of $Ru_3(CO)_{12}$**2**, as a potential *in situ* route to $H_2Ru_3(CO)_{10}$.



Scheme 2.2: New synthetic route to $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5** (i) reaction with $Me_3NO\text{-}CH_2Cl_2$ in presence of 1,3 C_6H_8; (ii) heating in hexane

The compound $Ru_3(CO)_{12}$**2** may be directly activated towards reaction with 1,3 cyclohexadiene with trimethyl amine N-oxide in dichloromethane at -78°C (Scheme 2.2). Two major products have been obtained and separated by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture. By comparison with previously obtained spectroscopic data, the compounds have been characterised as $HRu_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_6H_7)$ and $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**5**. There is no doubt that this new one-step synthetic route to compound **5** is considerably more convenient than that previously employed. Problems encountered while synthesising the *bis*-acetonitrile compound $Ru_3(CO)_{10}(MeCN)_2$ can now be by passed. It has also been found that the dienyl complex can be converted into the benzene compound **5**, simply by heating in hexane, thus providing an alternative route to the inconsistent steps of the original synthesis (Scheme 2.1, steps (iii) and (iv)).

The mechanism by which this sequence of reactions occurs is not altogether clear, but a postulated mechanism involves the formation of the highly reactive cluster $H_2Ru_3(CO)_{10}$ as a key intermediate. The reaction of $Ru_3(CO)_{12}$**2** with Me_3NO in dichloromethane in the absence of 1,3 cyclohexadiene produces good yields of the tetrahydrido-tetraruthenium cluster $H_4Ru_4(CO)_{12}$ as the only identifiable product. This observation is consistent with the suspected reaction sequence given below (Scheme 2.3)



Scheme 2.3: Proposed reaction sequence for the synthesis of $H_4Ru_4(CO)_{12}$

In contrast to the reactions of $Ru_3(CO)_{12}$**2**, $Os_3(CO)_{12}$**1** does not react in the same way. However, reaction of the activated cluster $Os_3(CO)_{10}(MeCN)_2$ **3** with 1,3 cyclohexadiene in dichloromethane affords one major product which was initially

formulated on the basis of spectroscopic data as $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6**. The mass spectrum exhibits a parent peak at 928 amu (calc:-930) followed by the sequential loss of at least ten carbonyl groups. The ^1H nmr spectrum indicates the cyclohexadiene moiety is bound to one metal atom displaying signals at δ 5.27, 3.77 and 1.86 ppm with relative intensities of 1:1:2. This is consistent with the previously reported spectroscopic data for compound **6**.[3]

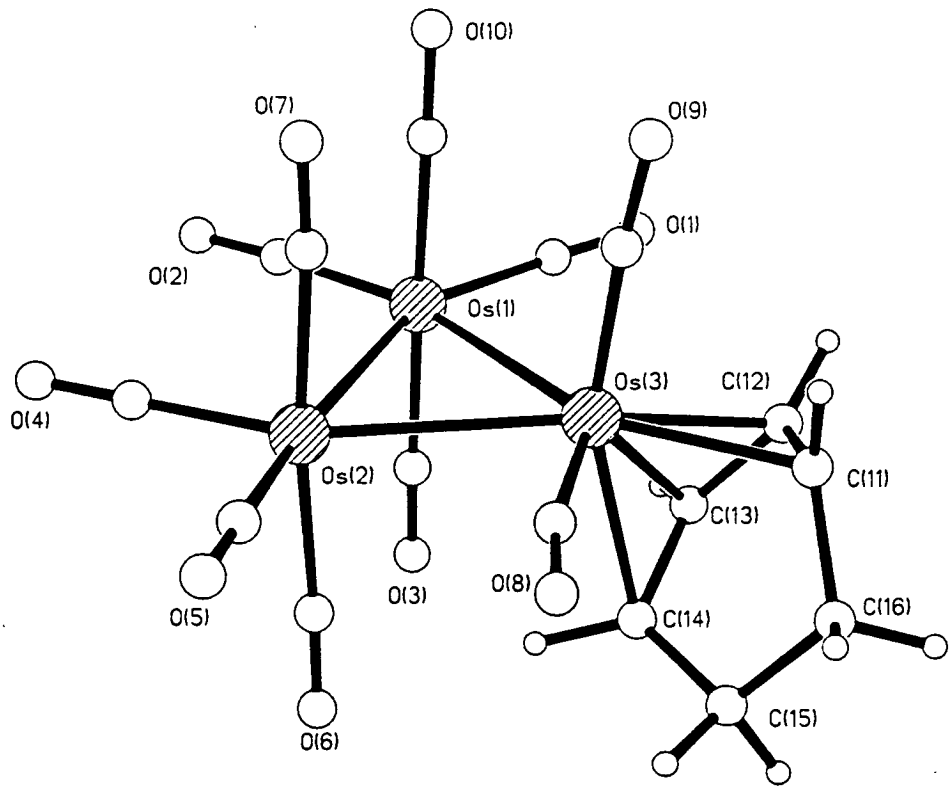


Figure 2.2: The solid state molecular structure of $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** showing the atomic labelling scheme. Relevant bond lengths(Å): Os(1)-Os(3) 2.8884(9), Os(1)-Os(2) 2.8645(9), Os(2)-Os(3) 2.8790(9), Os(3)-C(11) 2.203(18),Os(3)-C(12) 2.342(16), Os(3)-C(13) 2.203(18), Os(3)-C(14) 2.245(18), C(11)-C(12) 1.48(3) , C(11)-C(16) 1.52(3) , C(12)-C(13) 1.44(3), C(13)-C(14) 1.49(2), C(14)-C(15) 1.47(2), C(15)-C(16) 1.50(16), mean Os-C (CO) 1.92(2), mean C-O 1.13(2).

The molecular structure of $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** has been established and is depicted in Figure 2.2 together with some relevant bond lengths. Crystals suitable for single crystal X-ray analysis were obtained from a toluene solution at -30°C. The osmium atoms define a regular triangle with mean metal-metal bond length 2.88Å, this is similar to that reported for the parent carbonyl cluster $Os_3(CO)_{12}$**1**. The

cyclohexadiene ligand is η^4-bound to Os(3) in an equatorial-axial co-ordination mode, having replaced two carbonyl groups. The diene displays a boat confirmation with a mean Os-C distance of 2.25Å. The ten carbonyl ligands are terminally bound, four each to Os(1) and Os(2) and two to Os(3).

The compound $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** can be converted to the dienyl cluster $HOs_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^1\text{-}C_6H_7)$ in low yield on heating in octane under reflux. The dienyl cluster may then be readily converted to compound **4** by the previously established means. This method offers no significant advantage over the route already established.[1,11]

The isolation of compound **6** is however of some interest. Recent work on the related chemistry of hexa- and penta-ruthenium carbido clusters have shown that benzene may adopt terminal and face-capping co-ordination modes.[12,13] On the basis of detailed structural analysis, it has been proposed that the benzene ligand will adopt a face-capping co-ordination when the diene precursor adopts an $\mu_2{:}\eta^2{:}\eta^2$- bridged orientation between two metal centres. Thereby, proving an attractive route first to a face-capping dienyl and then to a face-capping benzene. However, this hypothesis does not appear to apply to trinuclear clusters.

On the basis of these observations it has been postulated that the reaction of $Ru_3(CO)_{10}(MeCN)_2$ with 1,3 cyclohexadiene proceeds via a similar intermediate *viz* $Ru_3(CO)_{10}(\eta^4\text{-}C_6H_8)$, but that this intermediate is less stable than the corresponding osmium compound, eliminating a CO ligand to form the co-ordinatively unsaturated intermediate "$Ru_3(CO)_9(\eta^4\text{-}C_6H_8)$", which then undergoes C-H bond cleavage to generate the known dienyl complex.

2.3 Preparation of substituted 1,3 cyclohexadiene ligands†

The reduction of aromatic compounds by alkali metals in liquid ammonia represents a highly efficient and convenient method for the preparation of partially unsaturated six membered rings. The reaction was initially discovered by Wooster and Godfrey[14], although the major development resulted from the efforts of Birch[15] and the reaction has since come to bear his name. Several excellent review articles concerned with the theoretical aspects and synthetic applications are available.[16,17]

† The synthesis and characterisation of some of the compounds reported in the following sections was carried out in conjunction with Dr S.L. Ingham at The University of Edinburgh.

The most commonly used metals are lithium or sodium, although a variety of metals may be employed. Lithium has both a higher molar solubility and higher reduction potential in ammonia than sodium or potassium,[18] and reactions are frequently cleaner than those of heavier metals. The apparent superiority of lithium is a consequence of several factors, lithium salts are generally less soluble than other counterparts and lithium shows a weaker tendency to undergo iron-catalysed side reactions with alcohols.[19]

Alkali metals dissolve in liquid ammonia to produce deep blue solutions that behave as if they contain metal cations and solvated electrons, thus providing an excellent reducing medium. As shown in Figure 2.3, an electron is accepted by the aromatic to produce a radical anion in equilibrium with the reactant. In the presence of an alcohol, the radical anion may be protonated to furnish a radical which quickly adds an electron resulting in a monoanion. Further protonation results in the isolation of the reduced species required.

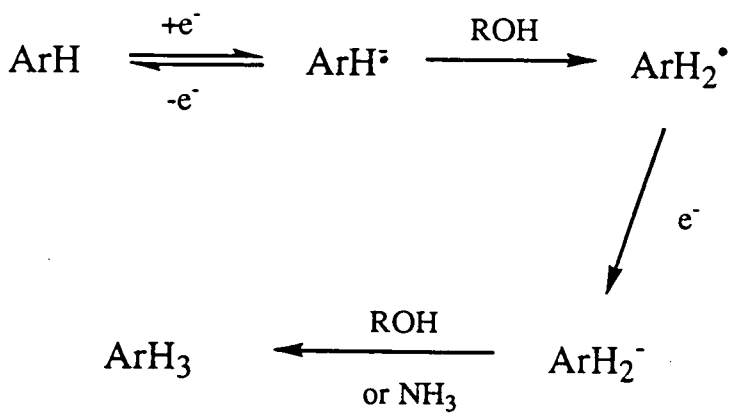


Figure 2.3: Mechanism for the reduction of aromatic compounds

The Birch reduction of benzene derivatives generally gives rise to non-conjugated 1,4 cyclohexadienes, where "electron-donating substituents" direct reduction so that the major product has the maximum number of such groups attached to the residual double bonds, according to the "Birch Rule".[16]

Unfortunately, 1,4 cyclohexadienes do not react well with triosmium clusters and a method for the isomerisation to 1,3 cyclohexadienes was required. A number of transition metal complexes are known to produce double bond isomerisation,[20] although, this is frequently accompanied by complex formation. Birch reported the use

of Wilkinson's catalyst $(Ph_3P)_3RhCl$ for the successful isomerisation of 1-methoxy-1,4 cyclohexadiene to 1-methoxy-1,3 cyclohexadiene by heating under reflux in chloroform for two hours.[21] However, this reaction does not appear to work for methyl substituted 1,4 cyclohexadienes and it would therefore appear that the substituent may have an influence on the mechanism and formation of 1,3 dienes.

The reaction of 1,4 cyclohexadienes with iron pentacarbonyl to yield 1,3 cyclohexadiene iron tricarbonyl complexes is well known.[22] The reactions were initially carried out either with tri-iron dodecacarbonyl in refluxing benzene or by *ultra violet* irradiation with iron pentacarbonyl in benzene. Later studies have demonstrated that heating the 1,4 cyclohexadiene with iron pentacarbonyl under reflux in dibutyl ether, gives greatly improved yields.[23] This method has been employed for all isomerisations described within this chapter.

The mechanism proposed for the formation of conjugated diene-iron complexes from non-conjugated dienes was reported by Cristol and Lee and is depicted in Figure 2.4.[24] An allylic hydrogen abstraction mechanism has been confirmed by labelling the methylene groups with deuterium and analysing the deuterium product.

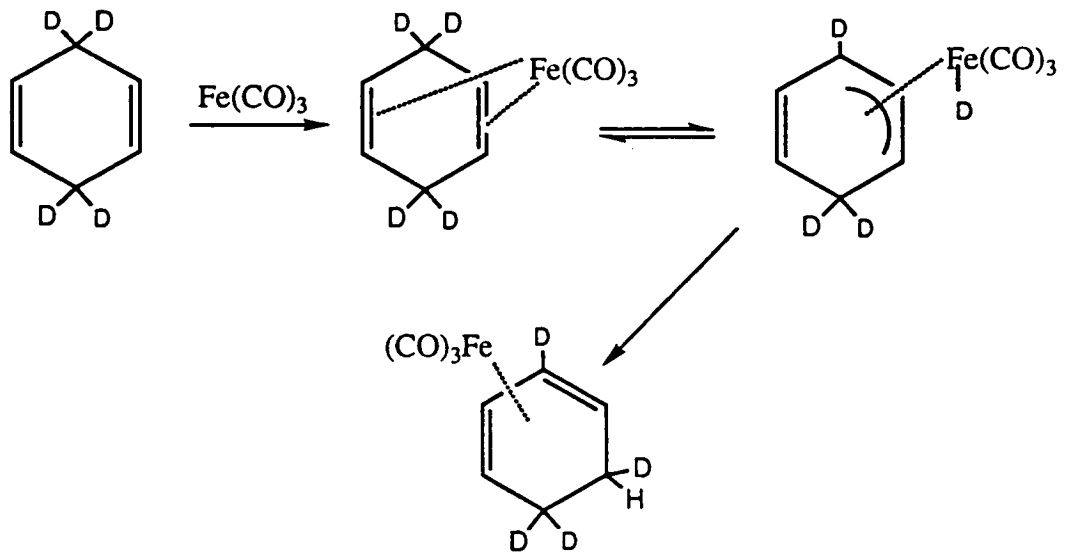


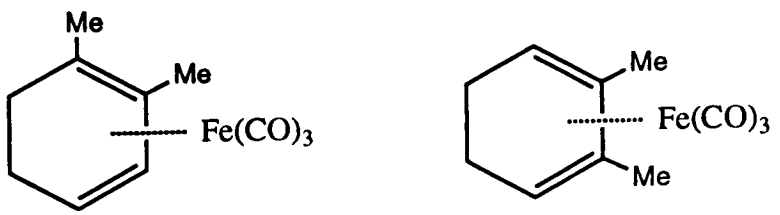
Figure 2.4: The proposed mechanism for the isomerisation of 1,4 dienes into 1,3 dienes

In order to carry out reactions with the 1,3 cyclohexadiene ligands, it is necessary to disengage the organic fragment from the iron carbonyl complex. A simple and relatively mild procedure involves the use of trimethyl amine N-oxide.[25] However, this

reaction has proven inefficient and an alternative was required. The use of cupric chloride for the efficient removal of $Fe(CO)_3$ groups in ethanol provided a useful alternative.[26] Although this reaction was extremely effective it proved to be rather messy. The method that has been employed for the disengagement of all the substituted 1,3 cyclohexadienes prepared herein involves the oxidation of the complex using Ceric ammonium nitrate,[27] unless otherwise stated. All 1,3 cyclohexadiene ligands prepared contained a mixture of isomers and were used directly.

2.4 Preparation of $Os_3(CO)_{10}(\eta^4\text{-}o\text{-}Me_2C_6H_6)$8

The 1,4 cyclohexadiene obtained from the Birch reduction of *ortho*-xylene has been reacted with iron pentacarbonyl in dibutyl ether under reflux for 24 hours. The orange oil obtained has been characterised on the basis of spectroscopic data as $Fe(CO)_3(o\text{-}Me_2C_6H_6)$**7**. The IR spectrum of compound **7** displays three strong bands in the metal carbonyl stretching frequency. The mass spectrum exhibits a parent peak at 248 amu (calc:-248). Two isomeric possibilities for compound **7** are depicted in Figure 2.5



I II

Figure 2.5: The isomeric possibilities for $Fe(CO)_3(o\text{-}Me_2C_6H_6)$7

The ^1H nmr spectrum displays six signals in total, two singlets at δ 1.65 and 2.13 ppm, a doublet at δ 5.10 ppm and three multiplets at δ 2.94, 1.80 and 1.58 ppm with relative intensities 3:3:1:1:2:2, this is indicative of isomer I.

Disengagement of the organic ligand from the $Fe(CO)_3$ unit has been achieved by oxidation with cerium ammonium nitrate. The reaction of the free ligand with $Os_3(CO)_{10}(MeCN)_2$**3** in dichloromethane for four hours affords one major product, which has been formulated as $Os_3(CO)_{10}(\eta^4\text{-}o\text{-}Me_2C_6H_6)$**8** on the basis of the IR spectrum. The spectrum is almost identical in the CO stretching region to $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6**.[28] The mass spectrum exhibits a parent peak at 964 amu (calc:-959) followed by the sequential loss of at least ten carbonyl groups, this corroborates

with the IR evidence. The ^{1}H nmr spectrum of compound **8** can be seen in Figure 2.6, detailed assignment has been made possible by a series of decoupling experiments. The doublet at δ 6.11 ppm shows coupling to the signal at δ 3.35, these may be attributed to the olefinic protons A and B respectively. Signal B also shows coupling to the aliphatic protons at δ 1.72 ppm (C), which in turn shows coupling to the signal at δ 2.01 ppm (D). On this basis the spectrum was assigned. The $^{13}C\{^{1}H\}$ nmr spectrum also confirms the presence of only one isomer.

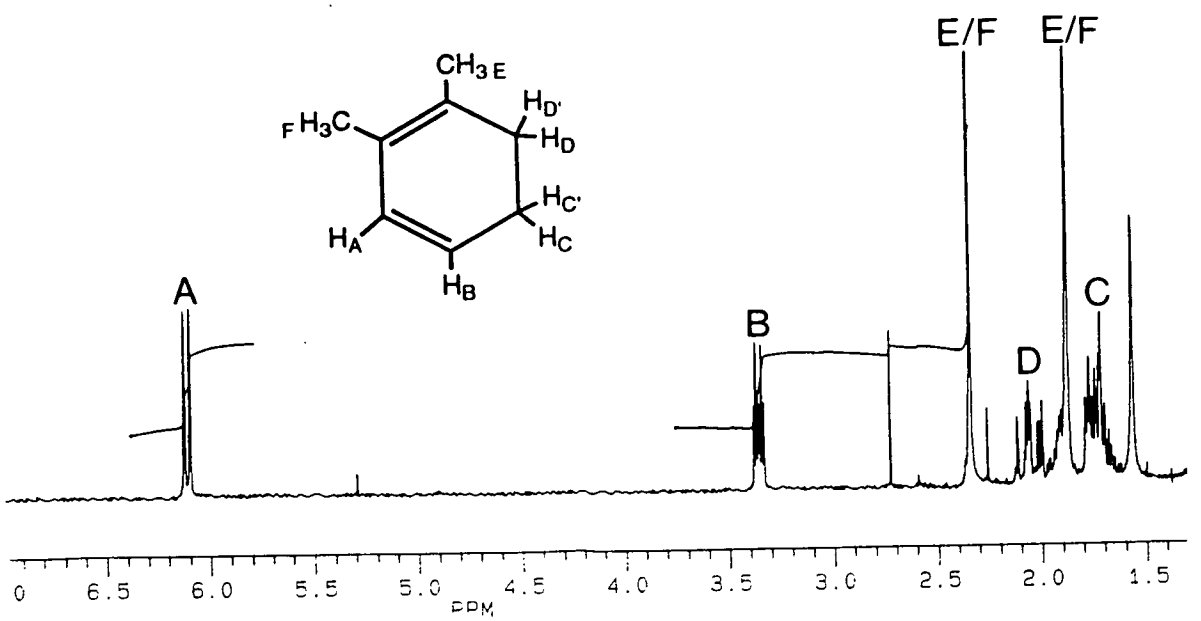
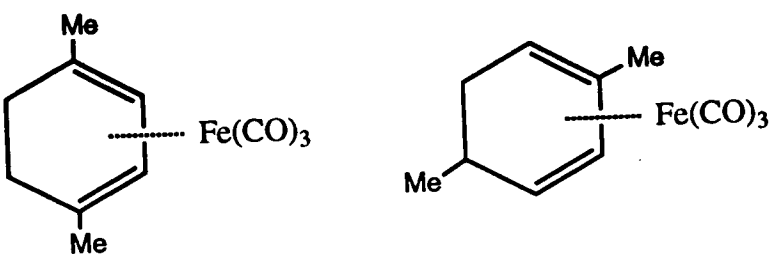


Figure 2.6: The ^{1}H nmr spectrum of $Os_3(CO)_{10}(\eta^4\text{-}o\text{-}Me_2C_6H_6)$**8**

2.5 Preparation of $Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$10

The iron compound $Fe(CO)_3(p\text{-}Me_2C_6H_6)$**9** has been prepared by the reaction of iron pentacarbonyl with the 1,4 cyclohexadiene obtained from the Birch reduction of *para*-xylene as described in Section 2.4.



I
60%

II
40%

Figure 2.7: The isomeric possibilities for $Fe(CO)_3(p\text{-}Me_2C_6H_6)$**9**

Compound **9** was initially characterised by comparison of the IR spectrum with that of compound **7** and found to be in good agreement in the CO stretching region. The mass spectrum exhibits a parent peak at 248 amu (calc:-248). Unfortunately the ^{1}H nmr spectrum could not be obtained and the $^{13}C\{^{1}H\}$ nmr spectrum showed the compound to be a complex mixture of isomers. The previously reported synthesis for compound **9** has shown that the two isomeric possibilities depicted in Figure 2.7 exist in the ratio 60:40.[29]

Disengagement of the organic ligand can be achieved by reaction with cerium ammonium nitrate. The free ligand can then be reacted with $Os_3(CO)_{10}(MeCN)_2$**3** in dichloromethane at room temperature to afford two products, which may be separated by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture. The products have been characterised in order of elution as $Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$**10** and $HOs_3(CO)_{10}Cl$. The mass spectrum of compound **10** exhibits a parent peak at 964 amu (calc:- 959) followed by the consecutive loss of carbonyl groups. The ^{1}H nmr spectrum shown in Figure 2.8, indicates that the minor isomer has co-ordinated to the cluster core. A detailed assignment has been made possible by a series of decoupling experiments. The results of which are listed in Table 2.1.

Signal	δ ppm	Intensity	Coupling responses
A	6.20 d	1H	B
B	3.30 dd	1H	A, D
C	0.96 d	3H	D
D	2.05 m	1H	B, C, E, F
E	1.54 m	1H	D, G
F	2.37 td	1H	D, G
G	3.68 dt	1H	E, F
H	2.35 s	3H	—

Table 2.1: Assignment of ^{1}H nmr signals for $Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$**10**

It is not possible to assign the aliphatic protons E and F explicitly from the decoupling experiments, but their assignment may be proposed on the basis of their

proximity to the metal cluster. Thus the multiplet at δ 2.37 ppm is attributed to the M-*exo* proton F and the M-*endo* proton E gave rise to the signal at δ 1.54 ppm.

From the ^1H nmr spectrum traces of another isomer can be observed. This can be explained by the co-ordination of the opposite face of the cyclohexadiene ring. The methyl groups occupying the 3,6 positions as opposed to the 2,5 positions on the diene ligand. However, no evidence has been observed for the co-ordination of the major isomer I, possibly due to steric restraints.

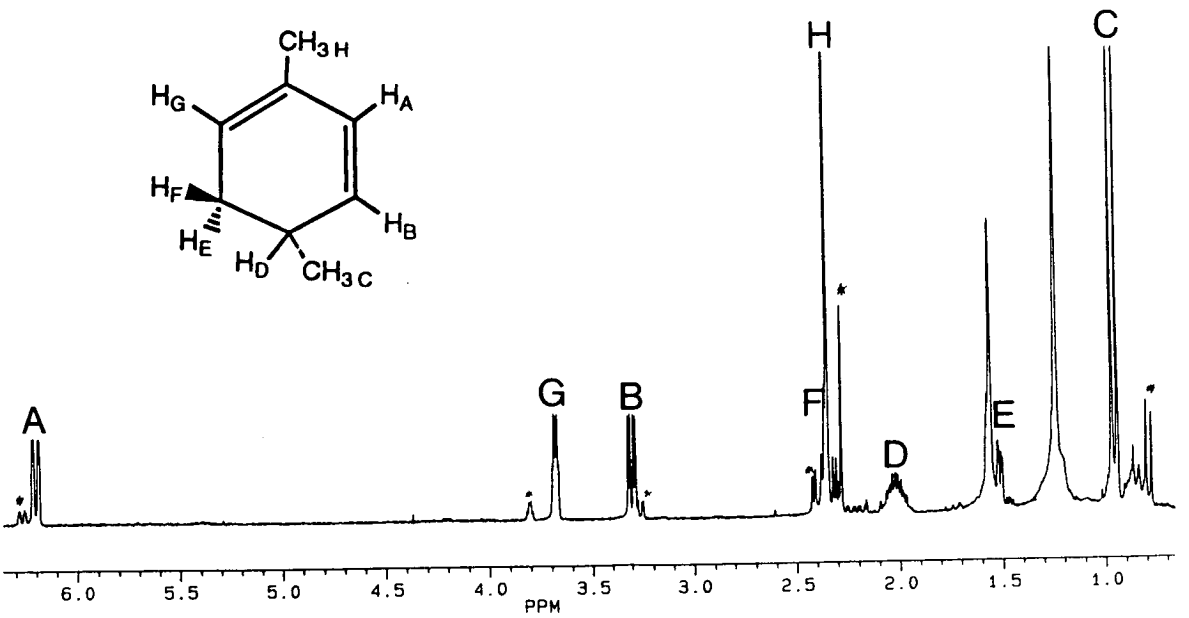


Figure 2.8: The ^1H nmr spectrum for $Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$**10**

Computer simulations for the proposed molecular structures of compound **10** are shown in Figure 2.9. This pictorial representation has been achieved by the manipulation of the atomic co-ordinates obtained from the X-ray crystal analysis of the unsubstituted diene complex $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6**.[28] By extrapolation of the C-H bond from 1.08Å to 1.58Å (C-C single bond distance), the co-ordinates of a methyl carbon atom can be determined attached to any carbon atom within the cyclohexadiene ring. The hydrogen atoms can then be added using the HADD command in the XP molecular graphics program.[30] It must be stressed that this method is by no means accurate or reliable, it simply provides an indication of the steric interactions that may be encountered by the cyclohexadiene moiety, offering an explanation as to why the major isomer I does not co-ordinate to the cluster.

As can be shown from the values listed above a methyl group in the 4-position of the cyclohexadiene ring interacts strongly with an adjacent carbonyl group displaying a very short bond contact of 1.52Å. Contacts in the 3,6-positions and 2,5-positions with adjacent carbonyl groups are slightly longer and these steric interactions may explain the inability of the major *para*-$Me_2C_6H_6$ isomer to co-ordinate to the cluster.

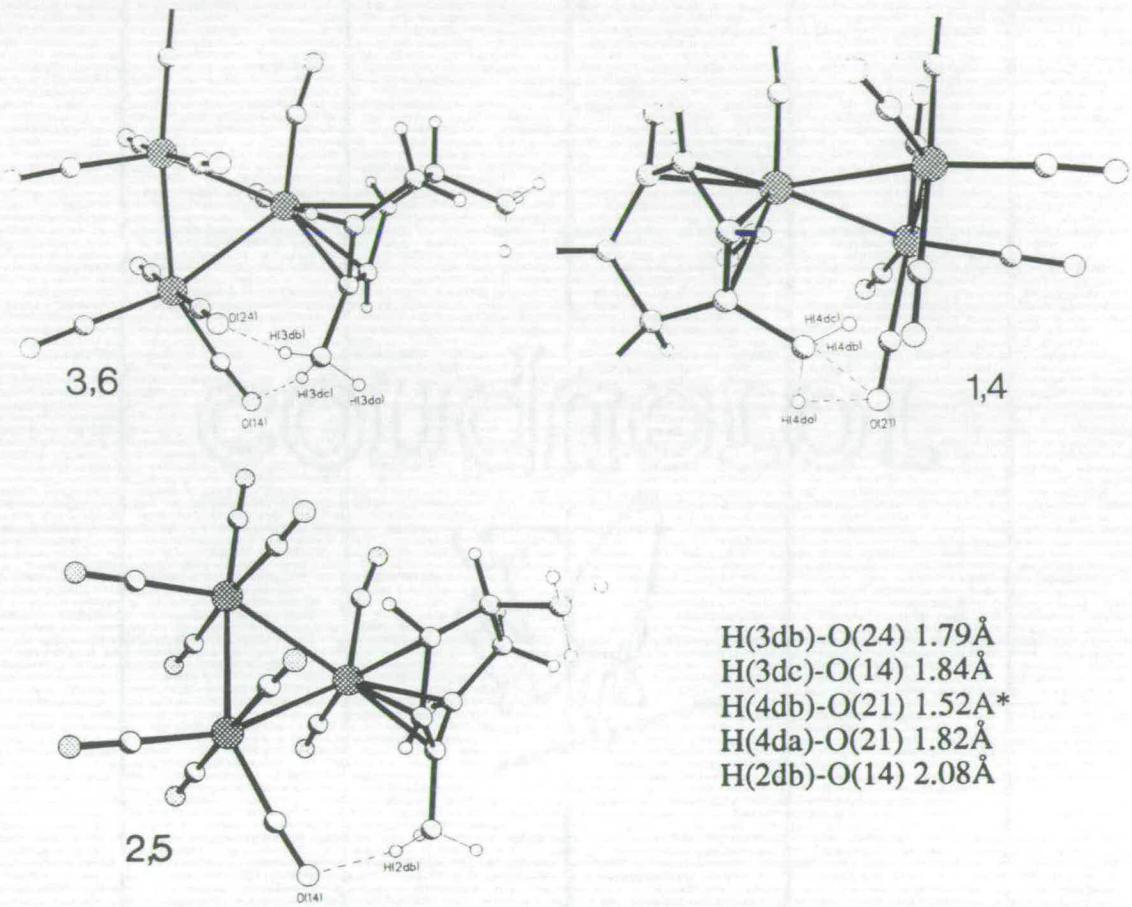


Figure 2.9: Predicted molecular structures of $Os_3(CO)_{10}(\eta^4\text{-}p\text{-}Me_2C_6H_6)$**10**

2.6 Preparation of some other triosmium diene complexes

2.6.1 Characterisation of $Os_3(CO)_{10}(\eta^4\text{-}m\text{-}Me_2C_6H_6)$**12**

The compound $Fe(CO)_3(m\text{-}Me_2C_6H_6)$**11** has been prepared in a similar manner to the iron compounds previously reported. Formulation of compound **11** was achieved by comparison with previously obtained spectroscopic data. The ^1H nmr spectrum of compound **11** displays a complex mixture of isomers. The free ligand can be reacted with $Os_3(CO)_{10}(MeCN)_2$**3** to afford one major product, characterised on the basis of spectroscopic data as $Os_3(CO)_{10}(\eta^4\text{-}m\text{-}Me_2C_6H_6)$**12.** From the ^1H nmr spectrum one isomer can be seen to have co-ordinated. Detailed assignment has been made possible

by a series of decoupling experiments, the results of which are listed in Table 2.2. The isomer co-ordinated to the cluster core is shown alongside Table 2.2.

Signal	δ ppm	Intensity	Coupling responses
A	4.92 d	1H	B
B	5.95 dd	1H	A, C
C	3.54 dd	1H	B
D	2.21 m	1H	E, G
E	0.97 d	3H	D
F	2.34 m	1H	—
G	1.54 m	1H	D
H	1.81 s	3H	—

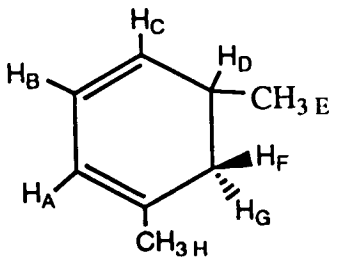
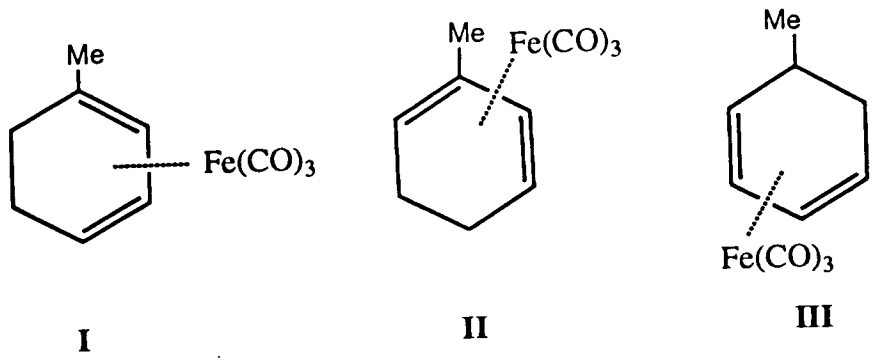


Table 2.2: Assignment of ^{1}H nmr signals for $Os_3(CO)_{10}(\eta^4$-*m*-$Me_2C_6H_6)$**12**

The olefinic protons A, B and C can be ascribed to the signals at δ 4.92, 5.95 and 3.54 ppm on the basis of their coupling responses. The signal at δ 0.97 ppm clearly couples to the signal at δ 2.21 ppm, these have been ascribed to the protons of the methyl group E and the aliphatic proton D respectively. The singlet at δ 1.81 may be attributed to the protons from the methyl group H. The remaining two signals at δ 2.34 and 1.54 ppm must arise from the aliphatic protons F and G. Although it is not possible to assign these explicitly from the decoupling experiment, their assignment has been proposed on their proximity to the metal. Thus the M-*exo* proton F gives rise to the signal at δ 2.34 ppm, while the M-*endo* proton G gives rise to the signal at δ 1.54 ppm. No evidence has been observed for the co-ordination of any other isomer.

2.6.2 Characterisation of $Os_3(CO)_{10}(\eta^4$-$MeC_6H_7)$**14**

The iron compound $Fe(CO)_3(MeC_6H_7)$**13** has been previously reported by Birch to contain a mixture of the three isomers shown in Figure 2.10.[29] The reaction of $Os_3(CO)_{10}(MeCN)_2$**3** with the free ligand affords one major product in high yields, which has been characterised as $Os_3(CO)_{10}(\eta^4$-$MeC_6H_7)$**14** on the basis of spectroscopic data. The ^{1}H nmr spectrum shows evidence for the co-ordination of three different diene isomers to the cluster core, full assignment of the ^{1}H nmr spectrum has proved impossible.



I II III

Figure 2.10: The isomeric possibilities for $Fe(CO)_3(MeC_6H_7)$13

2.7 An attempt to link two clusters

The preceding sections have demonstrated the ability of substituted 1,3 cyclohexadienes to co-ordinate to triosmium clusters. It was envisaged that these observations may provide a useful method for the linking of two cluster units. If a suitable diphenyl ligand could be partially reduced to form two 1,3 cyclohexadiene linked fragments, the possibility of linking two triosmium clusters may be realised.

The Birch reduction of 1,2 diphenylethane produces a white crystalline compound. The ^1H nmr spectrum displays four signals at δ 2.07, 2.64, 5.43 and 5.70 ppm with relative intensities 2:4:1:2, no aromatic protons were observed. The $^{13}C\{^1H\}$ nmr spectrum confirmed the production of one symmetrical isomer. Isomerisation of the 1,4 $C_{14}H_{18}$ ligand has been achieved by reaction with iron pentacarbonyl in dibutyl ether, heating under reflux for 24 hours. The yellow oil obtained has been formulated as $Fe_2(CO)_6(C_{14}H_{18})$**15** on the basis of spectroscopic data. The IR spectrum is reminiscent of those previously observed for iron tricarbonyl 1,3 diene complexes. The mass spectrum exhibits a parent peak at 466 amu (calc:-466) indicating that two $Fe(CO)_3$ units have successfully co-ordinated to the ligand. The ^1H nmr spectrum provides very little information displaying four signals at δ 1.53-1.74, 2.43-2.60, 3.10 and 5.21 ppm. The signals are extremely broad and signal overlap made interpretation difficult. The $^{13}C\{^1H\}$ nmr spectrum provides more information displaying three $\{CH_2\}$ signals at δ 23.6, 24.7 and 39.5 ppm, three {CH} signals at δ 59.2, 64.9 and 85.5 ppm and one quaternary carbon signal {C} at 105.1 ppm. This indicates that one isomer which is symmetrical in nature has been produced. The proposed structure of which is shown in Figure 2.11.

The disengagement of the organic ligand can be achieved by reaction with cupric chloride in ethanol at room temperature overnight. The resulting solution can be

extracted with hexane and dried over sodium sulphate (anhydrous) to yield the 1,3 $C_{14}H_{18}$ ligand.

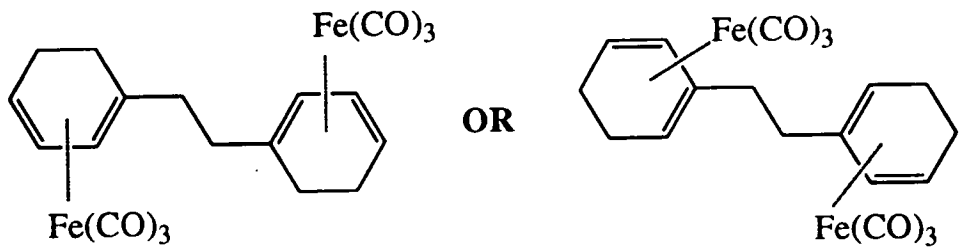


Figure 2.11: The isomeric possibilities for $Fe_2(CO)_6(C_{14}H_{18})$**15**

The reaction of the free ligand with $Os_3(CO)_{10}(MeCN)_2$**3** in dichloromethane for four hours afforded two major products. The products can be separated by tlc eluting with a dichloromethane/hexane (1:9 v/v) mixture. Unfortunately only one compound has been characterised. On the basis of spectroscopic data the compound has been formulated as $Os_3(CO)_{10}(\eta^4\text{-}C_{14}H_{16})$**16**. The second product observed isomerises quickly to compound **16**. The mass spectrum of compound **16** exhibits a parent peak at 1032 amu (calc:- 1034) followed by the sequential loss of ten carbonyl groups. This indicates that the ligand has co-ordinated to only one cluster.

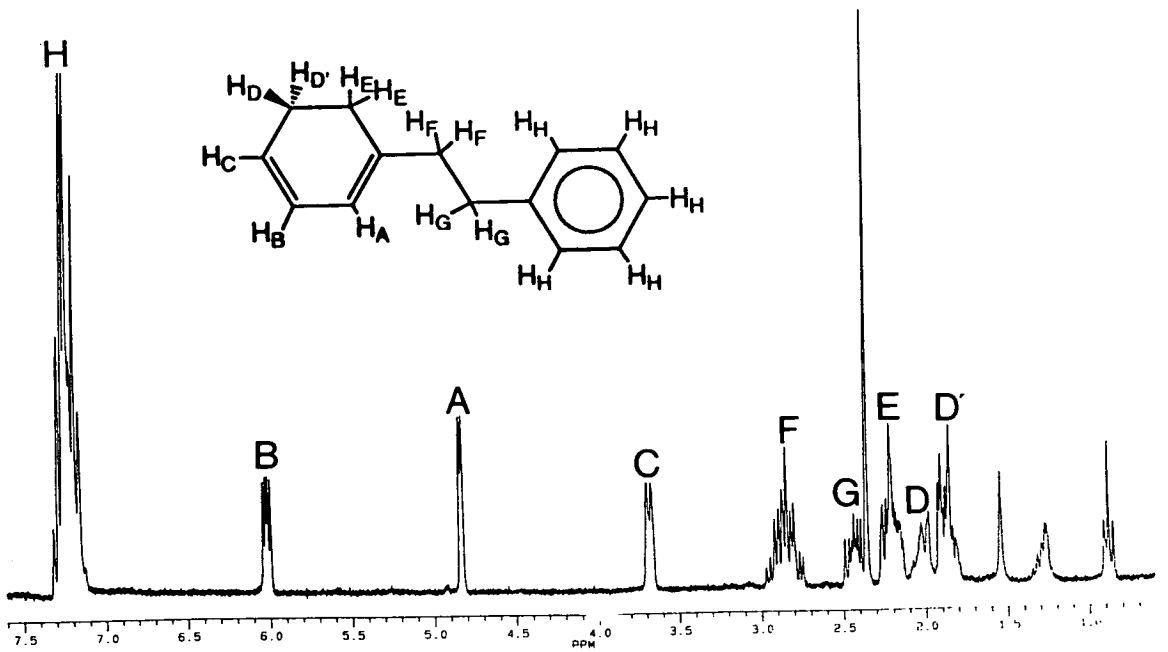


Figure 2.12: The ^{1}H nmr spectrum of $Os_3(CO)_{10}(\eta^4\text{-}C_{14}H_{16})$**16**

The ^1H nmr spectrum of compound **16** can be seen in Figure 2.12, full assignment has been made possible by a series of decoupling and nOe experiments. Clearly from the ^1H nmr spectrum, evidence for the rearomatisation of the unco-ordinated end of the diphenyl can be observed. The multiplet at δ 7.11-7.32 can be attributed to the aromatic protons H. The olefinic protons A, B and C can be ascribed to the signals at δ4.84, 6.02 and 3.68 ppm, on the basis of coupling responses. These proton signals are very characteristic of the olefinic protons for a substituted 1,3 diene co-ordinated to a cluster, both in frequency and multiplicity. The signals at δ 2.02 and 1.88 ppm have been attributed to the aliphatic protons M-*exo* D and M-*endo* D'. M-*exo* D displays a slight coupling to signal C, while M-*endo* D' displays a coupling response to the signal at δ 2.20 ppm, E. This assignment has been confirmed by nOe responses. The signals at δ 2.42 and 2.85 ppm have been ascribed to the aliphatic protons F and G. Both signals display coupling and nOe responses to each other. Signal F also displays nOe responses to signals A and E. On this basis the ^1H nmr spectrum has been assigned.

To date, the linking of two triosmium clusters has not been achieved. The contributing factor appears to be the tendency of the reduced diphenyl ligand to rearomatise at one end. This problem may be overcome by increasing the chain length within the diphenyl, using ligands such as diphenylpropane or diphenylbutane. Unfortunately, due to time constraints, these reactions have not as yet been investigated.

2.8 Concluding remarks

The reaction of trimethyl amine N-oxide with carbonyl clusters is proving to be an extremely attractive and convenient method of producing highly reactive intermediates in the formation of diene and arene cluster complexes. The new one step synthetic route for the preparation of the face-capping benzene cluster $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$**5** offers a surprisingly simple and highly efficient alternative to the already established synthetic route. It may be of interest to carry out the reaction of $Ru_3(CO)_{12}$**2** with Me_3NO in the presence of 1,3 substituted dienes, in an attempt to synthesise a wide range of face-capping arene clusters.

The ability of substituted diene ligands to co-ordinate to triosmium clusters has been established. These complexes may prove extremely useful if a synthetic method converting them to the corresponding face-capping arene can be found. The possibility of linking two triosmium clusters using partially reduced diphenyl ligands shows great potential and the further reactions should be investigated.

2.9 References

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Chapter 3:-A route to a Triosmium *bis*-benzene cluster

This chapter commences with a brief introduction to the substitution chemistry of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and includes an example of benzene migration in a triosmium cluster. The successful synthesis of the *bis*-benzene cluster $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ is reported, the benzene ligands occupy different bonding modes, one terminally bound, the other capping the triosmium face. The *bis*-benzene cluster is prepared in a stepwise manner through a series of benzene-diene complexes. These intermediate compounds undergo interesting isomerisation reactions and fluxional behaviour, both of which are discussed in detail. The use of trimethyl amine-N-oxide as a decarbonylation reagent is highly successful due to a low co-ordination ability. The synthesis of $H_2Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$ is reported, this compound is a rare example where the amine group co-ordinates to a triosmium cluster. Finally reactions involving a range of substituted cyclohexadiene ligands are discussed in brief.

3.1 Introduction

The carbonyl substitution chemistry of the face capping benzene cluster $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4** is similar to that of the parent dodecacarbonyl cluster $Os_3(CO)_{12}$**1**, where thermally promoted reactions proceed rather inefficiently and with low selectivity.[1] A technique employed throughout transition metal chemistry involves the prior replacement of a CO group for a more 'labile' ligand such as acetonitrile, which can subsequently be displaced by the appropriate ligand. This strategy has been applied to compound **4** and the activated benzene cluster $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)$**17** has been isolated from the reaction of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4** with Me_3NO in acetonitrile.[2] Treatment of **17** with further Me_3NO leads predominantly to cluster decomposition. A range of two electron donors such as CO, PR_3 and alkenes can readily replace the labile acetonitrile forming equatorially substituted derivatives $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(L)$ where the benzene moiety retains a face-capping co-ordination.

The molecular structure of $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$**18** is shown in Figure 3.1.[3] The structure is based upon that of the triosmium benzene starting compound **4** with one equatorial carbonyl being replaced by a π-bound ethylene ligand. The stability of the ethylene complex $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$ **18** differs from the π-adduct of the parent dodecacarbonyl $Os_3(CO)_{11}(\eta^2\text{-}CH_2CH_2)$ **19**. Where as solutions of **18** in dichloromethane are not air-sensitive, compound **19** is

highly labile in the absence of external ethylene and can be easily converted on thermolysis to the hydride- vinylidene species $H_2Os_3(CO)_9(\mu\text{-}CCH_2)$[4]. It would appear that the greater basicity of the $Os_3(CO)_8(C_6H_6)$ fragment relative to the $Os_3(CO)_{11}$ moiety accounts for this reactivity difference; the stability of the metal-olefin interaction being enhanced in $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$**18** due to more extensive π-back donation.

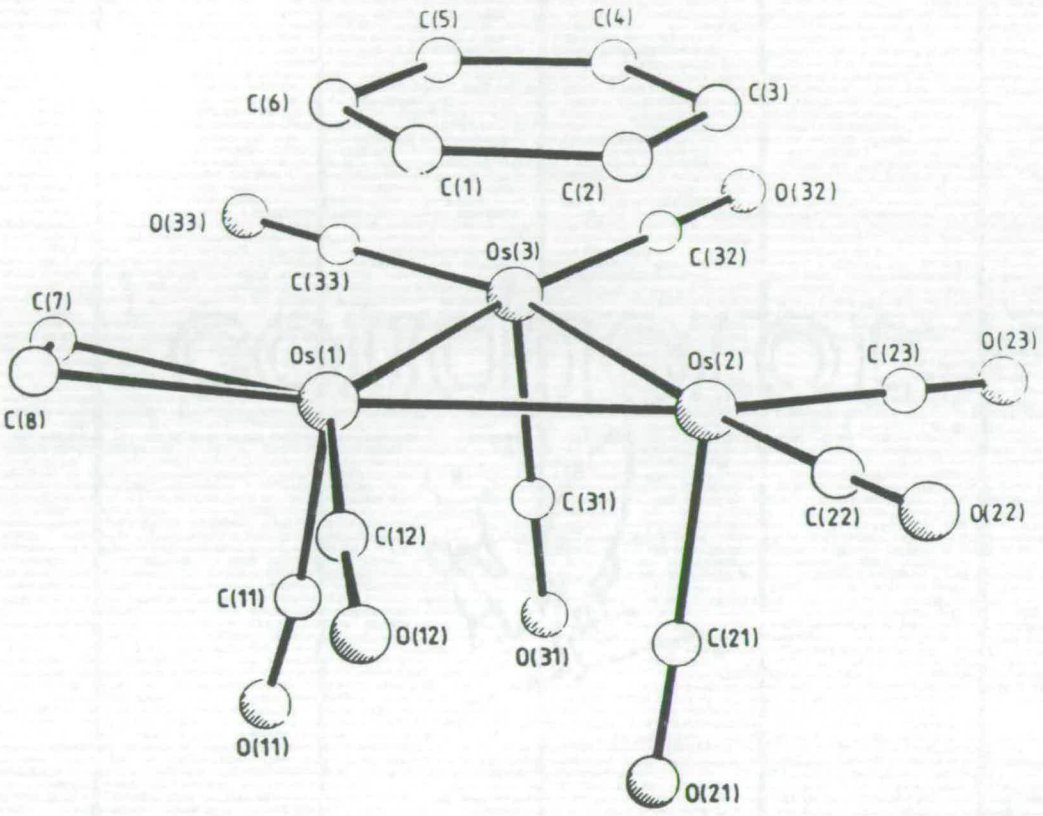
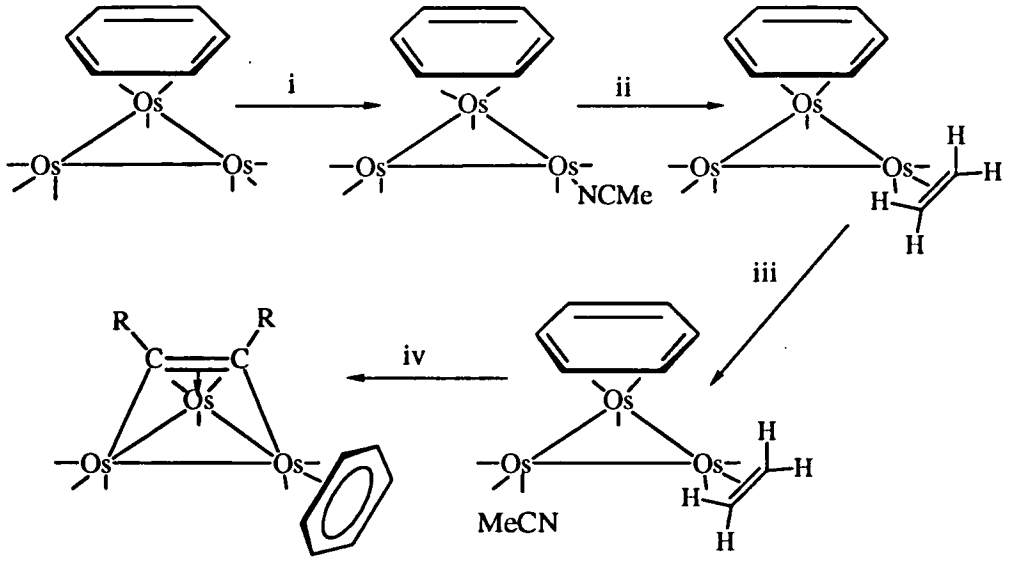


Figure 3.1: The molecular structure of $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$ **18**

The compound $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$**18** undergoes further substitution(Scheme 3.1) by reaction of Me_3NO/MeCN to give the activated cluster $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)(MeCN)$. This compound can then be reacted with a range of alkynes ($RR'C_2$) to form the complexes $Os_3(CO)_7(\eta^6\text{:-}C_6H_6)(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_2RR')$ [R=R'=H,Ph or Me: R=H R'=Ph; R=Me R'=Et] in which the benzene has migrated to a μ-terminal position and is bound to a single metal allowing the alkyne to span the triangulo-face.[5]

In contrast the ruthenium analogue $Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$**5** does not as readily undergo substitution reactions. However direct reaction with alkynes affords the cluster $Ru_3(CO)_7(\eta^6{-}C_6H_6)(\mu_3{:}\eta^2{-}RC_2R'CO)$ similar to the osmium complex, except that a carbonyl group has been inserted between one of the Ru-C σ bond of the alkyne.[6]



Scheme 3.1: Stepwise preparation of $Os_3(CO)_7(\eta^6{-}C_6H_6)(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1{-}C_2RR')$ (i) Me_3NO-CH_2Cl_2-MeCN; (ii) C_2H_4; (iii) Me_3NO-CH_2Cl_2-MeCN; (iv) C_2R_2

3.2 Preparation of benzene-diene clusters

Treatment of a freshly prepared solution of $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(MeCN)$**17** in dichloromethane with 1,3 cyclohexadiene results in the formation of one major product, which on the basis of mass spectroscopic data has been formulated as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}C_6H_8)$**20** . The mass spectrum exhibits a parent peak at 952amu (calc:-953) followed by the consecutive loss of several carbonyl groups. Verification of the benzene-diene cluster **20** was based on the comparison of the infra red spectrum of **20** with previously synthesised η^2-alkene compounds such as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}CH_2CH_2)$ and $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}CH_2CHPh)$.[7] The IR spectra in the CO stretching region were in good agreement and the cyclohexadiene moiety can be thought of as being bonded in an η^2-fashion as a mono-ene. The ^1H nmr spectrum in $CDCl_3$ contains a broad singlet at δ3.88ppm, indicative of a face-capping benzene and a series of signals in the region δ5.92-0.87ppm, corresponding to the diene moeity. Unfortunately a well

resolved spectrum could not be obtained and complete assignment has proved impossible.

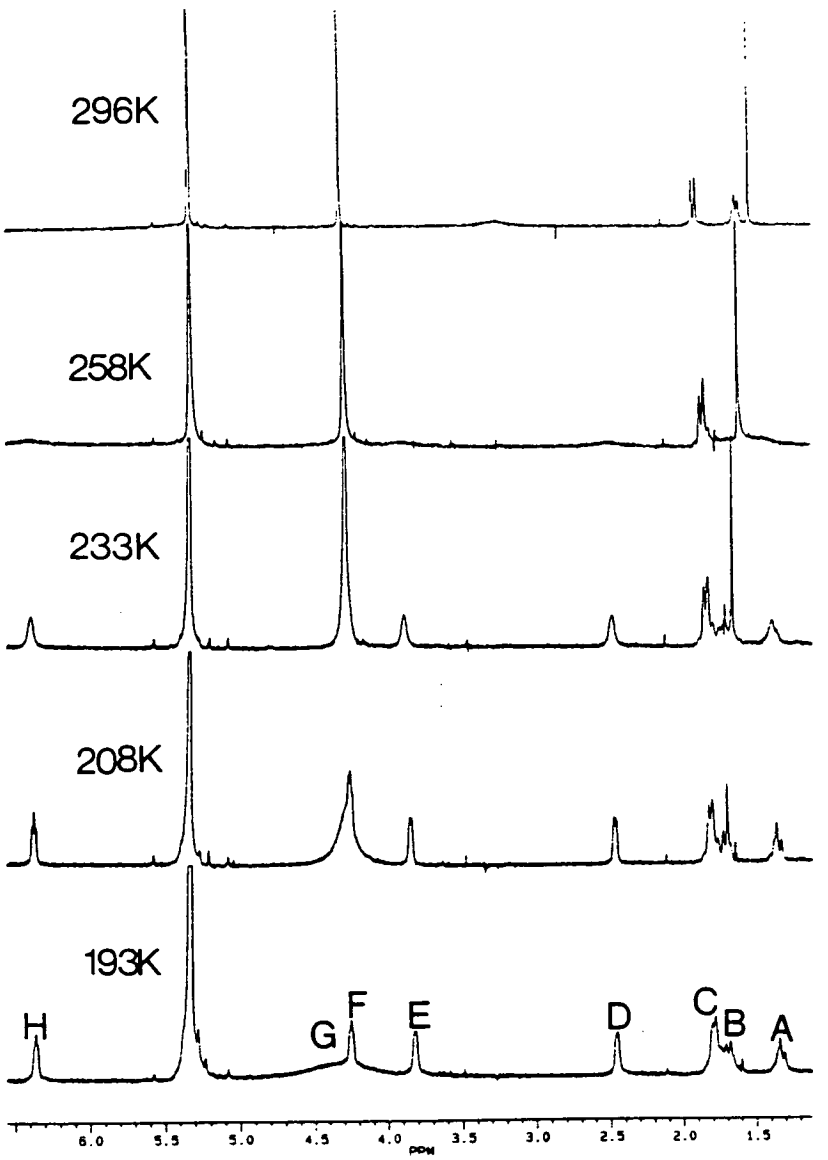
Cyclohexadiene has previously been observed to co-ordinate in an η^2 fashion in the tetraosmium cluster $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$[8]. The compound can be prepared in a similar fashion from the reaction of $Os_4(\mu\text{-}H)_4(CO)_{11}(MeCN)$ with 1,3 cyclohexadiene in CH_2Cl_2. A single crystal X-ray analysis of $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$ has been attempted, however the molecular structure could not be fully rationalised because of the disorder observed, although the cyclohexadiene ligand was clearly seen to bond as a mono-ene.

Further treatment of $Os_3(CO)_8(\mu_3\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20** with Me_3NO at room temperature appears to have no effect. However on heating to 40°C for 3 hours, a colour change from yellow to orange in the solution is observed. Isolation of the products by tlc eluting with a mixture of dichloromethane/hexane(3:7 v/v) results mainly in recovery of $Os_3(CO)_8(\mu_3\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20** starting material, some decomposition and one minor orange product. The orange product was characterised initially by spectroscopic techniques as $Os_3(CO)_7(\mu_3\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** . A parent peak in the mass spectrum at 927amu (calc:-925) was followed by the sequential loss of seven carbonyl groups. A change from η^2 to η^4 has been observed for the diene ligand. As a CO is lost, additional electron pair donation from the C_6 fragment occurs.

The ^1H nmr spectrum of compound **21** in CD_2Cl_2 exhibits a singlet at δ4.28ppm, indicative of a face capping benzene, however, the spectrum is unusually simple and the overall integrals are not consistent with the stoichiometry of the system. The system must therefore be undergoing some fluxional behaviour, the nature of which has been revealed by the acquisition of a series of ^1H nmr spectra at different temperatures in the range 296K-193K(Figure 3.2).

The spectrum at 193K comprises of eight signals labelled A-H, one of which G is very broad, but the integrals are now consistent with the expected number of hydrogens. Signals D and E, which are doublets at low temperature, arise from hydrogens which exchange sufficiently quickly at 296K to produce a broad signal at δ3.2, their multiplicities are consistent with them being from the H(1) and H(4) positions of an asymmetrically bound 1,3 cyclohexadiene. Similarly, the signals F and H undergo exchange which produces a broad signal at about the same δ value as the residual solvent ($CHDCl_2$) signal. These signals are narrow triplets and hence, assignable as the

H(2) and H(3) olefinic signals from the diene. The broad signal G, sharpens with increasing temperature to give a relatively tall sharp signal at 296K, as previously mentioned this signal is indicative of a face capping benzene, the rotation of which is sufficiently slowed at 193K to produce a broad signal. Such behaviour is not unprecedented and has been observed in the compound $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{-}\eta^2$ $C_6H_6)(\eta^2\text{-}CH_2CH_2)$**18**.[9] The signals A, B and C are consistent with the behaviour described above and are the aliphatic protons (H5-H6) of the diene, although full analysis of the spectrum has not been carried out.



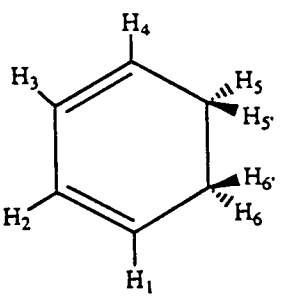
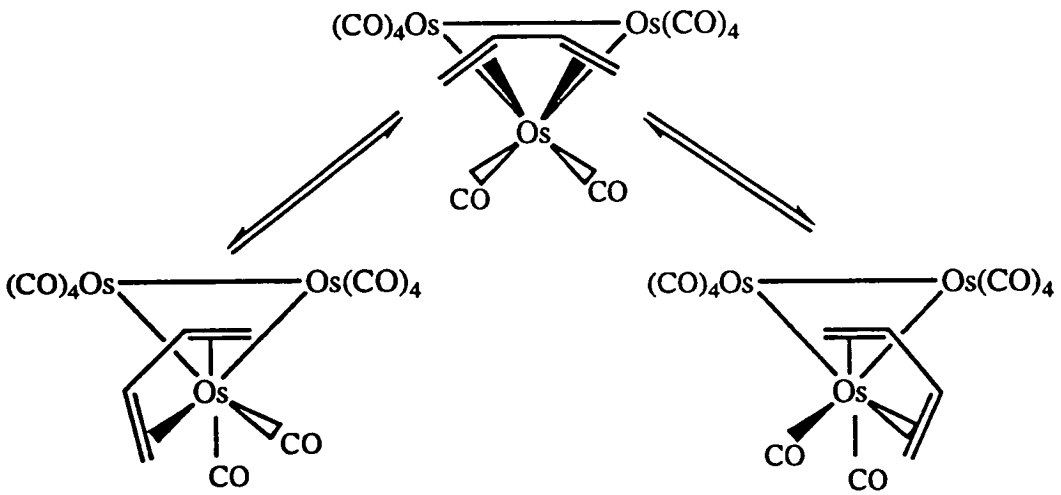


Figure 3.2: The variable temperature ^1H nmr spectra for compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** including the appropriate numbering scheme for 1,3 cyclohexadiene.

Fluxionality of a coordinated cyclohexadiene has been previously reported in the compound $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)6$.[10] The proposed mechanism(Scheme 3.2) involves the rocking of the organic moeity above the plane of the osmium triangle about one axial and two equatorial coordination sites. This results in a mirror plane through the organic ligand and is supported by the ^1H nmr data. However, for the compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** this mechanism would result in the production of an intermediate species in which the cyclohexadiene moeity is bound in an equatorial-equatorial fashion. This species is thought to be an isolatable product (section 3.3), therefore, rendering the mechanism invalid.

A postulated alternative mechanism involves the partial dissociation of the cyclohexadiene producing an intermediate species in which the diene is η^2- bound in an axial position. This intermediate allows the organic moeity to interchange between the two equatorial sites, creating a mirror plane through the ring system.



Scheme 3.2: Fluxionality of $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)6$

The molecular structure of compound **21** has been established and is shown in Figure 3.4 together with selected bond lengths. Crystals suitable for X-ray analysis were grown from a toluene solution at -30°C. The regular triangular arrangement of the osmium atoms has been preserved with metal-metal bond lengths of 2.834, 2.880 and 2.843Å. The benzene moeity is essentially planar, a distance of 2.16Å above the Os_3 triangle with an interplanar angle of 2.7°. The C_6H_8 ligand is η^4 bound to Os(2) occupying one axial and one equatorial bonding site. The diene displays a boat

conformation with a delocalised C4 system interacting with Os(2), mean Os-C distance 2.215Å, while the CH_2CH_2 fragment bends away from the cluster.

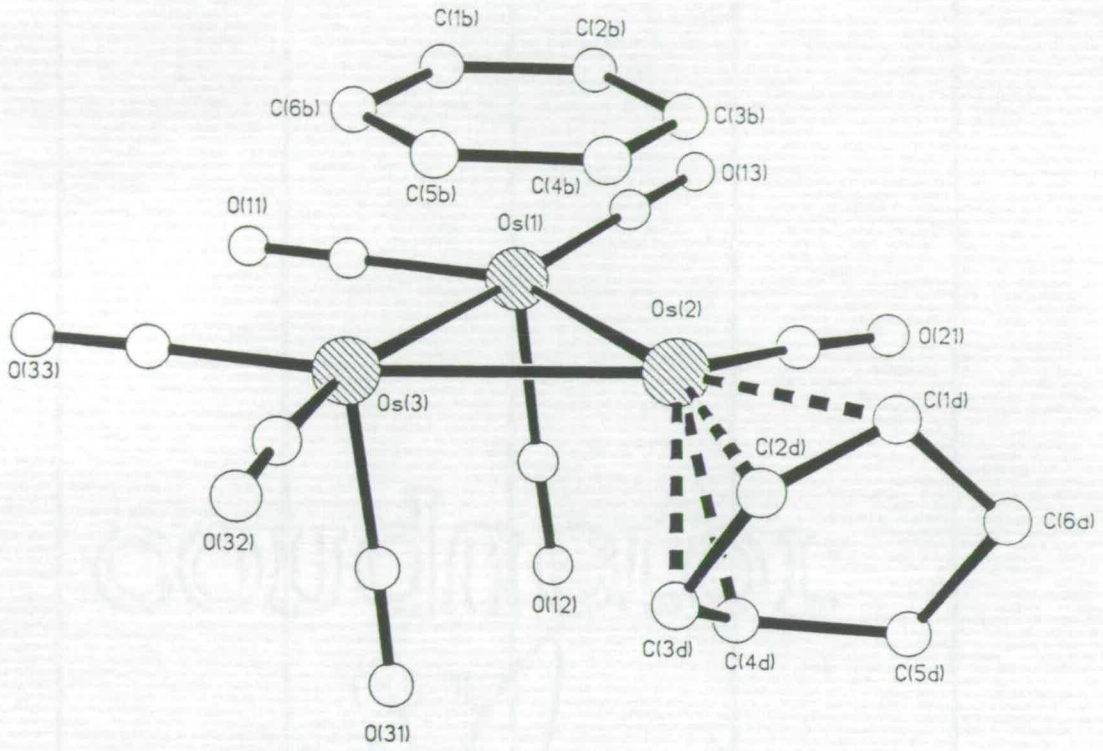


Figure 3.4:The solid state molecular structure of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å): Os(1)-Os(3) 2.843(3), Os(1)-Os(2) 2.834(3), Os(2)-Os(3) 2.880(2), Os(2)-C(1d) 2.205(10), Os(2)-C(2d) 2.178(10), Os(2)-C(3d) 2.222(10), Os(2)-C(4d) 2.256(9), Os(1)-C(1b) 2.229(8), Os(1)-C(2b) 2.301(8), Os(2)-C(3b) 2.230(9), Os(2)-C(4b) 2.231(9), Os(3)-C(5b) 2.329(8), Os(3)-C(6b) 2.275(9), C(1b)-C(2b) 1.403(13), C(1b)-C(6b) 1.475(14), C(2b)-C(3b) 1.470(13), C(3b)-C(4b) 1.419(13), C(4b)-C(5b) 1.443(13), C(5b)-C(6b) 1.40(2), C(1d)-C(2d) 1.414(14), C(1d)-C(6d) 1.495(14), C(2d)-C(3d) 1.42(2), C(3d)-C(4d) 1.431(14), C(4d)-C(5d) 1.522(14), C(5d)-C(6d) 1.57(2), mean Os-C (CO) 1.893(10), mean C-O 1.154(12).

A similar coordination of 1,3 cyclohexadiene has been observed in the compound $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6**[11]. The Os-C bond lengths for the facially coordinated arene range from 2.231 to 2.339Å. It is interesting to note that the benzene forms significantly shorter interactions with Os(2) {mean Os(2)-C 2.24Å}, than it does for the remaining two osmium atoms {mean Os(1,3)-C 2.33Å}. It seems likely that this slight asymmetry in the coordination of the facial benzene is due to the π-acceptor capability of the remaining ligands to which the metals coordinate. Both Os(1) and Os(3) have three

terminally bound carbonyl groups, whereas Os(1) has only one carbonyl group and the cyclohexadiene ligand. The latter ligand has a greatly reduced π-acceptor capability as compared with that of the carbonyl groups and as a result there is more electron density available on Os(2) for back donation into the π^* orbitals of the facially coordinated benzene. It is also of some note that the mean coordinated and uncoordinated C-C bond lengths within the benzene are 1.41Å and 1.46Å respectively, suggesting the possibility of a weak Kekulé type distortion, although high estimated standard deviations render this variation statistically insignificant.

3.3 Isomerisation of $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$21

The compound $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$**4** may be directly activated towards reaction with 1,3 cyclohexadiene upon treatment with an excess quantity of trimethyl amine N-oxide (Me_3NO) in dichloromethane at -78°C. On warming the reaction mixture to room temperature, an obvious colour change to bright yellow is observed. Extraction of the products by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture results in the formation of two yellow bands in approximately equal amounts. The first yellow band can be easily characterised as $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20**, by comparison with previously obtained spectroscopic data. The formulation of the second product remains tentative. The mass spectrum exhibits a parent peak at 926amu (calc:-925) followed by the sequential loss of seven carbonyl units, leading to the adoption of the formula $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(C_6H_8)$**22.** Compound **22** appears to be an isomeric form of compound **21**, with both compounds displaying characteristically different IR spectra. Two isomeric possibilities may be considered and are depicted in Figure 3.5.

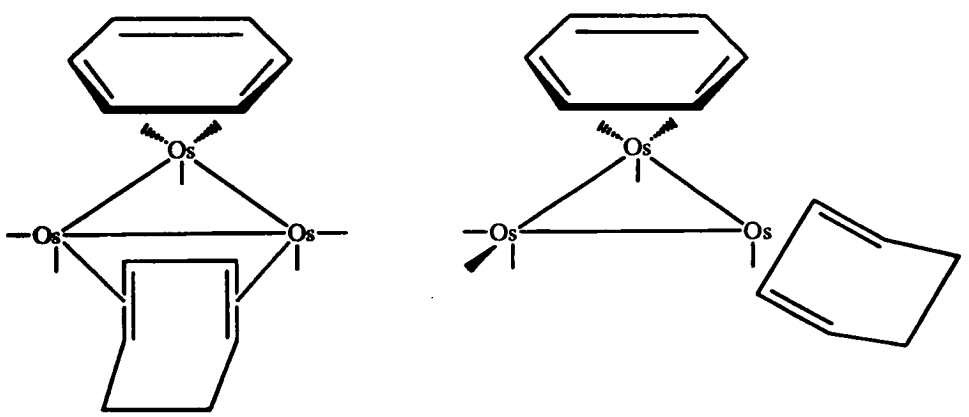


Figure 3.5- The isomeric possibilities for the compound $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(C_6H_8)$**22.**

The first involves the elimination of CO ligands from two different Os atoms, generating a vacant coordination site on each, which allows the cyclohexadiene to span an Os-Os edge, bonding in an μ_2:η^2:η^2-fashion. This type of coordination has been previously reported for higher nuclearity clusters such as $Ru_6C(CO)_{15}(\mu_2\text{-}C_6H_8)$[12] and $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8)$[13]. However, no examples of a bridging cyclohexadiene have been observed in tri- or tetra-osmium clusters to date. The second alternative results from the elimination of two equatorial carbonyl groups , whereas in compound **21** the cyclohexadiene occupies one axial and one equatorial bonding site, in this case the C_6 ring can be thought to ligate in an equatorial-equatorial fashion.

Conversion of compound **22** to $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** can be easily achieved by thermolysis in dichloromethane at 40°C for 4 hours. Alternatively the reaction can be carried out photolytically using a 500W tungsten-halogen lamp for 1 hour. In both cases separation of the products by tlc using a dichloromethane/hexane (4:6 v/v) mixture as eluents results in the isolation of one orange and one yellow product in equal yield.

Verification of the orange product as $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** was achieved by a comparison of the mass and ^1H nmr spectra with those previously obtained, both were found to be in good agreement. The yellow product was initially formulated on the basis of the spectroscopic data as $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23**. A parent peak in the mass spectrum was observed at 926amu (calc:-925) followed by the loss of several CO groups in succession, after which the fragmentation pattern became too complicated to observe any distinct ions.

The ^1H nmr spectrum of $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** displays twelve separate signals, labelled A-M as shown in Figure 3.6. Signals A and B are metal hydride signals at δ-20.78 and -16.32ppm respectively, each showing a relative integral of one proton. The remaining signals C-M are of relative intensities 1:2:2:1:1:1:1:1:1:1 respectively. Signals J-M may be assigned to the benzyne unit on the basis of both multiplicity and chemical shift, with the remaining six C-H signals arising from an asymmetrically bound diene moiety. Confirmation of the nature of the ligands and peak assignment were effected by carrying out a series of homonuclear decoupling and nOe experiments. Signals C and H, both of which are doublets of doublets comprise two couplings (ca 5.6Hz and 4.4 Hz in each case) can be assigned to the H(2) and H(3) olefinic diene positions. The decoupling experiments show that they not only couple to each other but signal C shows a coupling to signal F and signal H couples similarly to

signal G. Decoupling experiments carried out at signals F and G confirm these findings and also show that F and G are coupled with the D and E multiplets. Thus signals F and G correspond to the olefinic H(1) and H(4) protons and signals D and E to the aliphatic CH_2 protons of the diene. Interestingly signal G is also found to couple to signal B (ca 1.5Hz), one of the metal hydrides, which in turn shares a coupling with signal A (1.6Hz).

The nOe analysis of the system, in addition to showing enhancements consistent with the results of the decoupling experiments also provided a number of additional pieces of information. Firstly some inter-ligand nOe responses were found, most notably between the diene H(2)/H(3) protons and the benzyne H(1)/H(4) positions, as well as between the metal hydride signal, B and signal G. Secondly a number of saturation transfer responses were observed eg. between signals C and H, F and G and L and M. In addition there was a saturation transfer occuring between signals B and E. Clearly these findings are consistent with a fluxional process in the two ends of the benzyne moiety are exchanging, as are the two ends of the diene ligand, though these processes are still slow on the nmr timescale for discrete signals to be seen for each proton type.

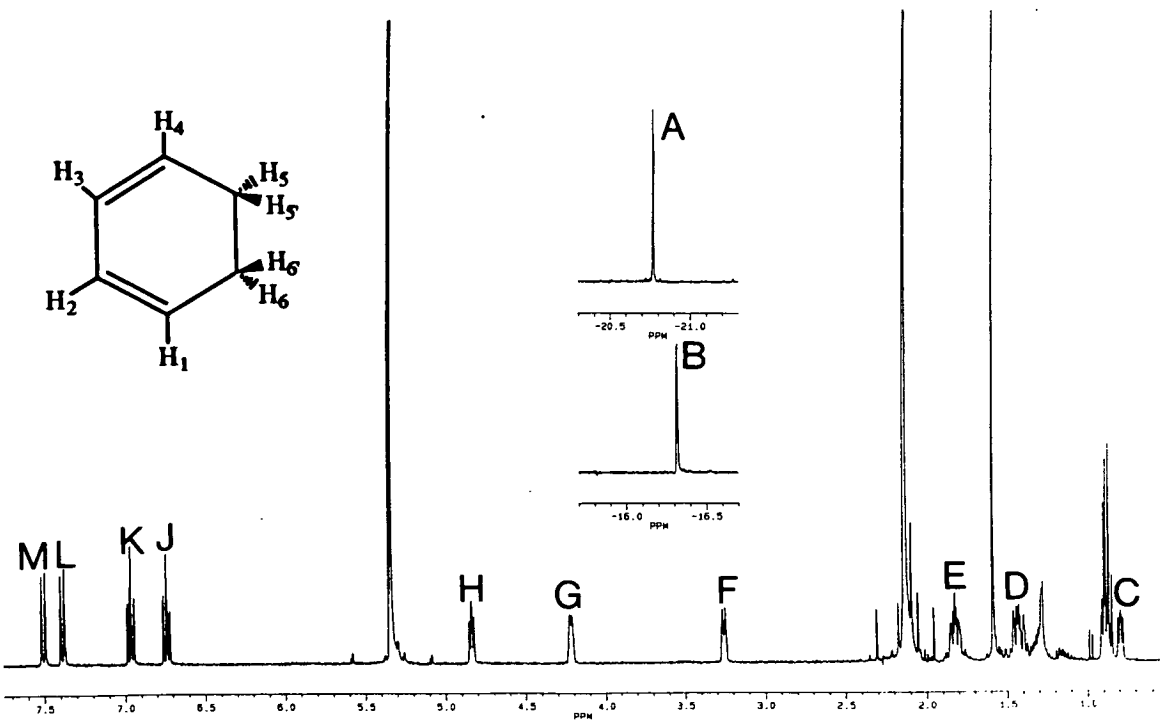
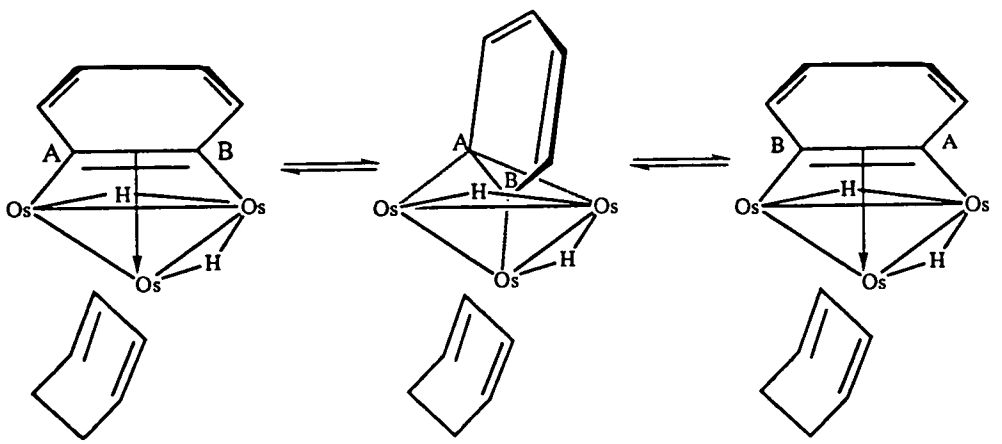


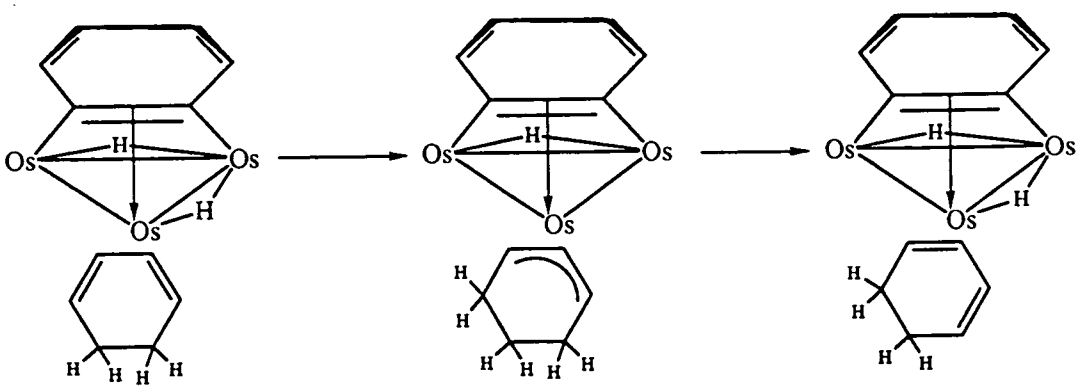
Figure 3.6: The ^1H nmr spectrum for compound $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$23

Two fluxional processes are postulated in Scheme 3.3. Process A demonstrates a ring rotation/flipping mechanism. This process allows the benzyne ligand to completely rotate with respect to the metal triangle without averaging the inequivalent hydride environments. The intermediate species in this mechanism displays a bonding mode that has been characterised crystallographically in the compound $Os_3(CO)_9(PEt)(C_6H_4)$[14], carbon B is σ bound to one osmium atom while carbon A bridges the other two metals.

Process A



Process B



Scheme 3.3: A. Rotation/Flipping of the benzyne ring. B. Reversible hydride migration to the cyclohexadiene

This process is a variation of the mechanism[15] proposed by Deeming for the compound $Os_3(CO)_7(\mu\text{-}AsMe_2)_2(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)$ in which rotation of the benzyne moeity equilibrates the two bridging arsenide ligands. In the nOe experiments, saturation transfer responses between signals L and M clearly demonstrate exchange of protons H(1)/H(4), this is consistent with a plane of symmetry through the benzyne ligand which results from the ring rotation/flipping mechanism proposed above.

Saturation transfer responses between the metal hydride signal B and signal E which has been attributed to the methylenic protons on the diene ring, indicates a relatively complex mechanism involving M-H/diene-H exchange. Whilst an involved study of the mechanism has not been undertaken, Process B represents an attempt to rationalise the nOe observations. The mechanism postulated involves an initial migration of the metal hydride to the cyclohexadiene ligand leading to the hydrogenation of the ring at the C(1) or C(4) positions. The intermediate species is an unsaturated 46 electron complex in which the C_6H_9 ring is bound to the Os unit in an π-allylic manner. Subsequent C-H bond cleavage of a methylenic proton, regenerates the 1,3 cyclohexadiene unit and a hydride migration to the cluster core leads to the reformation of a bridging hydride. This bridging hydride has previously been associated with the methylenic protons on the diene ligand and therefore would explain any averaging between the metal hydride signal B and the aliphatic protons of signal E in the nOe experiments. A similar process has been previously reported for π -cyclopentadienyl rhodium complexes containing 1,3 cyclohexadiene ligands. These compounds undergo proton exchange involving an interaction with the metal when in acidic conditions.[16]

The molecular structure of $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** has been confirmed by single crystal X-ray diffraction. Crystals suitable for analysis were obtained from a toluene solution at -30°C. The solid state structure is depicted in Figure 3.7, together with some relevant bond parameters. The osmium atoms define an irregular triangle with metal-metal bond lengths of 2.749, 2.866 and 3.024Å. As had been previously indicated by the spectroscopic data, the benzene ring has indeed undergone C-H bond cleavage and is bound to the cluster as a benzyne unit. Essentially a four electron donor the planar C_6H_4 fragment forms two σ bonds with Os(1) and Os(3) and undergoes a π -interaction with Os(2), to which it is inclined at an angle of 68°. The cyclohexadiene ligand is η^4-bound to Os(2) in an equatorial-equatorial coordination mode having replaced two carbonyl groups. The diene displays a boat confirmation, previously mentioned in section 3.2 with a mean Os-C distance of 2.20Å. The seven carbonyl ligands are terminally bound, three to each Os(1) and Os(3), with

one CO group attached to Os(2) occupying an axial site. The hydride ligands have not been located directly, through the distribution of the carbonyl ligands, one hydride may be thought to bridge the Os(1)-Os(3) edge, the Os-Os-C(carbonyl) angles being significantly wider (mean 107°). The other bridging hydride cannot be assigned conclusively.

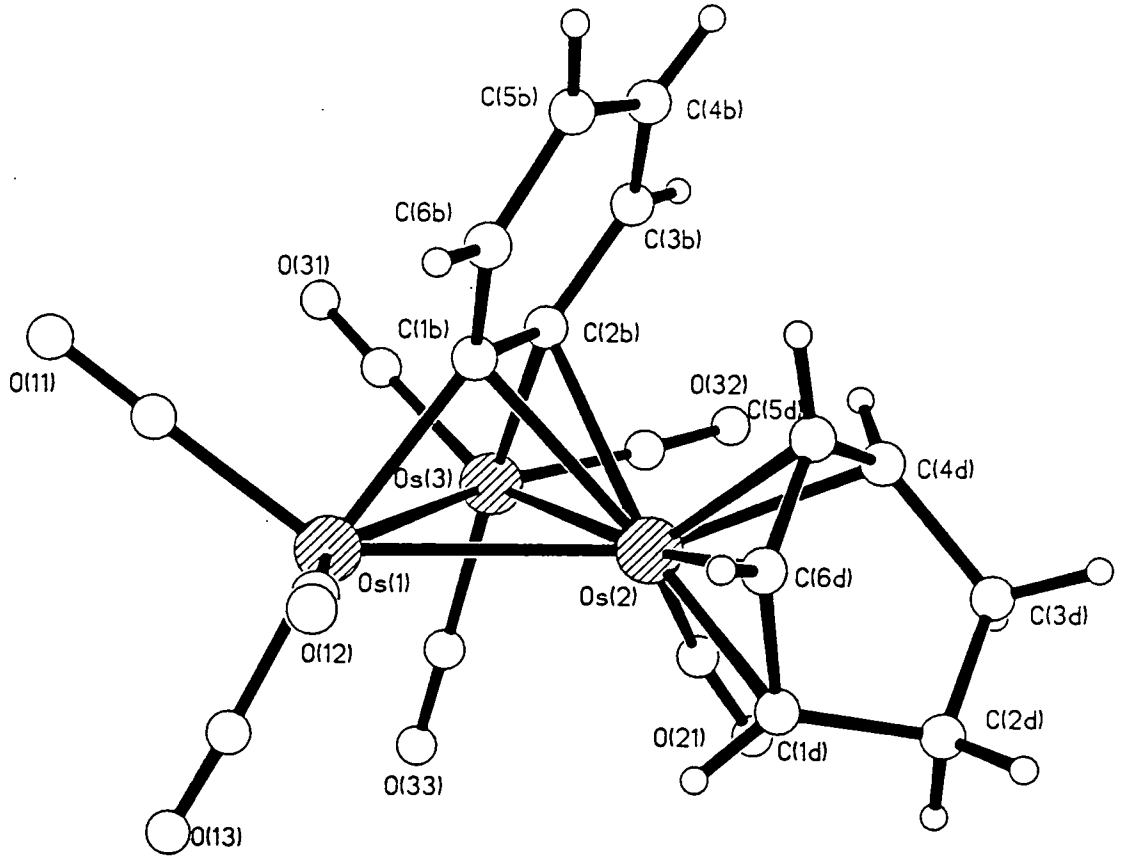
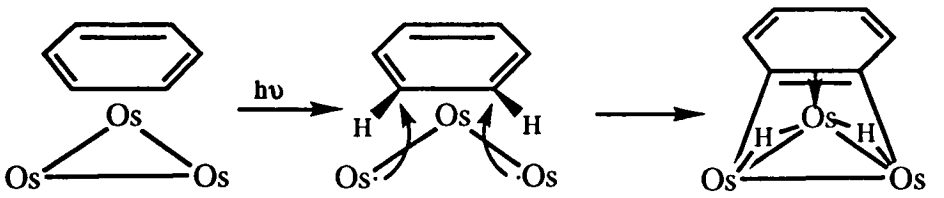


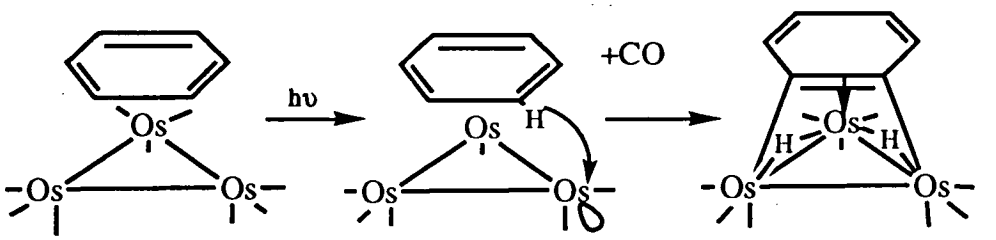
Figure 3.7:The solid state molecular structure of $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å): Os(1)-Os(2) 2.866(2), Os(1)-Os(3) 3.024(2), Os(2)-Os(3) 2.749(2), Os(2)-C(1d) 2.16(3), Os(2)-C(4d) 2.23(2), Os(2)-C(5d) 2.17(3), Os(2)-C(6d) 2.23(3), Os(1)-C(1b) 2.12(2), Os(2)-C(1b) 2.36(2), Os(2)-C(2b) 2.38(2), Os(3)-C(2b) 2.14(3), C(1b)-C(2b) 1.42(4), C(1b)-C(6b) 1.44(4), C(2b)-C(3b) 1.40(3), C(3b)-C(4b) 1.35(4), C(4b)-C(5b) 1.39(4), C(5b)-C(6b) 1.38(4), C(1d)-C(6d) 1.45(4), C(1d)-C(2d) 1.58(3), C(2d)-C(3d) 1.47(3), C(3d)-C(4d) 1.57(3), C(4d)-C(5d) 1.41(4), C(5d)-C(6d) 1.37(4), mean Os-C(CO) 1.90(2), mean C-O 1.16(2). Relevant bond angles(°): C(12)-Os(1)-Os(2) 96.5(6), C(11)-Os(1)-Os(3) 106.1(7), Os(2)-Os(1)-Os(3) 55.58(4), C(1b)-Os(2)-Os(3) 69.5(7), C(2b)-Os(2)-Os(1) 69.3(5), Os(3)-Os(2)-Os(1) 65.13(4), C(32)-Os(3)-Os(2) 93.6(8), C(31)-Os(3)-Os(1) 108.1(7), Os(2)-Os(3)-Os(1) 59.29(4).

The isomerisation of μ_3-benzene to μ_3-benzyne has been previously observed for the compound $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4**.[16] At 278K a toluene solution of compound **4** can be quantitatively converted into the isomeric triply bridging benzyne cluster $H_2Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)$ by irradiation with a 500W tungsten-halogen lamp for 13 hours. This reaction is thought to mimic the interconversion of the associatively and dissociatively chemisorbed states of benzene on low miller index surface planes of a metallic surface as previously discussed in section 1.4.

Homolysis of an Os-Os bond



Activation *via* CO dissociation



Non-dissociative activation

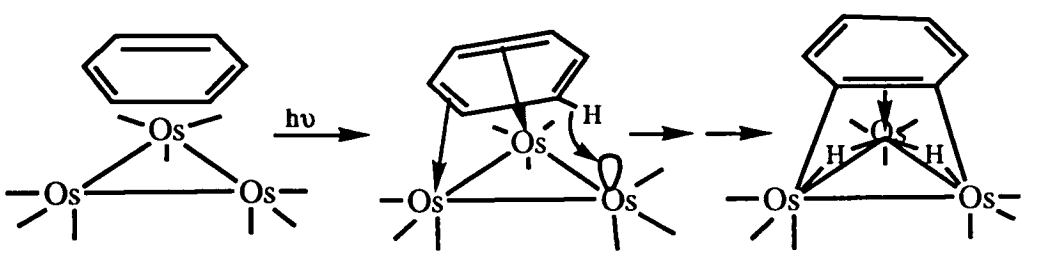
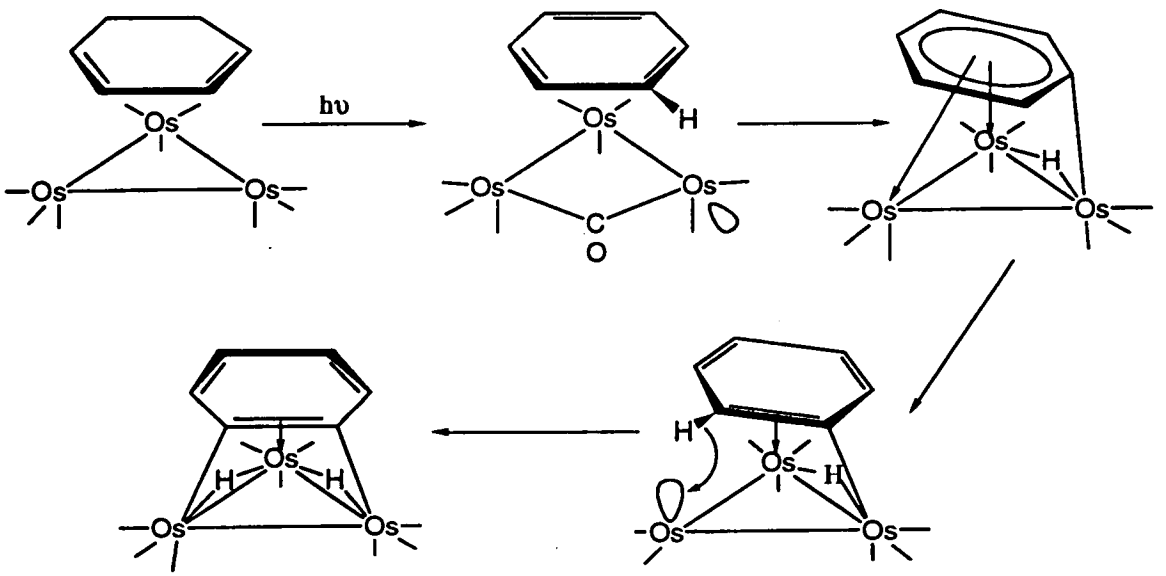


Figure 3.8:- Primary photoprocesses for the conversion of μ_3-benzene to μ_3-benzyne

The mechanism for the photolytic conversion of the μ_3-benzene to the μ_3-benzyne is not known. Several possibilities for the photochemistry have been suggested and are depicted in Figure 3.8. The first process involves the homolysis of an Os-Os bond and insertion of diradicals into two C-H bonds of the μ_3-benzene ligand. Subsequent rearrangement would generate the μ_3-benzyne compound.

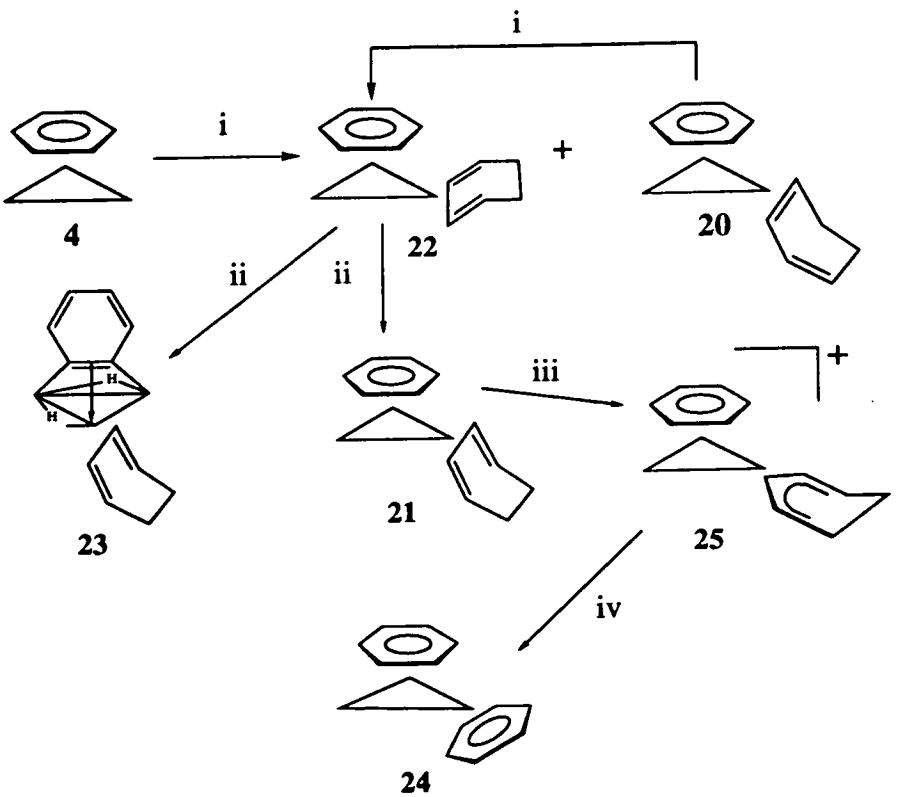
An alternative is the activation via CO dissociation. For compounds such as $Os_3(CO)_{12}$**1** and $Ru_3(CO)_{12}$**2**, photoinduced dissociative carbonyl loss is an important primary photoprocess.[18-20] The production of an electron deficient species through the loss of carbon monoxide activates the C-H bond on the benzene ligand. This process should be inhibited if the reaction is carried out in the presence of external carbon monoxide. However, the reaction proceeds as before and it seems unlikely that dissociative CO loss is directly relevant to the photochemistry of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4**. Non-dissociative activation via ring slippage could be a plausible elementary step in the photoisomerisation of compound **4**. The creation of a vacancy at the metal centre followed by metallation and subsequent rearrangement would afford the compound $H_2Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)$ Ring slippage of monometallic η^6-arene complexes is thought to play an important role in arene exchange reactions.



Scheme 3.4: Postulated mechanism for converion to $H_2Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)$

Perhaps, the most likely pathway for the photoisomerisation of $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\ C_6H_6)$**4** requires a vacancy formed by carbonyl insertion into an Os-Os bond as the primary photoprocess (Scheme 3.4). The first step is directly analogous to the formation of coordinatively unsaturated $M_3(CO)_{11}$, proposed by Wrighton[19] and Ford[20] to explain the associative substitution and fragmentation chemistry of $Os_3(CO)_{12}$**1** and $Ru_3(CO)_{12}$**2**. Metallation of the face capping ligand gives a π-aryl intermediate species. This species is similar to those recently implicated in a study of the ring to metal proton exchange in triosmium aryne complexes[21]. Subsequent ring slippage and metallation afford the benzyne complex as shown. The mechanism by which $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ **21** converts to $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** may be considered to be similar to the process proposed above.

3.4 Preparation and characterisation of the *Bis*-benzene cluster $Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}\ C_6H_6)(\eta^6\text{-}C_6H_6)$**24**



Scheme 3.5: The stepwise synthesis of $Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** from $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$**4**, (i) Me_3NO, XS 1,3 C_6H_8; (ii) heat; (iii) Ph_3CBF_4; (iv) DBU

The *bis*-benzene complex $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^6{-}C_6H_6)$**24** can be synthesised in a systematic stepwise manner from $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$**4**, the sequence of reactions is depicted in Scheme 3.5. As has been demonstrated in the preceding sections, treatment of compound **4** with trimethyl amine N-oxide (Me_3NO) in the presence of 1,3 cyclohexadiene generates the two compounds $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}C_6H_8)$**20** and $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(C_6H_8)$**22** The initial elimination of one carbonyl group creates a vacant coordination site on the surface of the cluster to which the diene can ligate in an η^2-fashion. This compound **20** can be converted into $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21** by reacting with Me_3NO, but only if excess 1,3 cyclohexadiene ligand is present. The excess ligand is assumed to stabilise any intermediate species formed during an elimination-addition process, in which the second double bond of the diene replaces a CO ligand.

The benzene-diene cluster **22** has been shown to easily undergo rearrangement to form two isomeric complexes. The first isomer results from a double C-H activation of the face-capping benzene to produce the benzyne-diene compound $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1{-}C_6H_4)(\eta^4{-}C_6H_8)$**23**. In the second complex $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21,** the benzene moeity retains a face capping coordination and the diene ring has migrated to an axial-equatorial orientation. Further treatment of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21,** with one molar equivalent of Me_3NO was expected to yield the *bis*-benzene compound $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^6{-}C_6H_6)$**24.** The removal of a CO ligand would generate a further coordination site on the cluster, it was envisaged that this would cause spontaneous C-H bond cleavage in the coordinated diene, the aromatic molecule having an enhanced stabilisation energy. However, major cluster decomposition resulted and no evidence for the *bis*-benzene cluster was observed.

The *bis*-benzene cluster **24** has been successfully prepared via a cationic benzene-dienyl intermediate. The reaction of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21** with trityl tetrafluoroborate $(Ph_3C)(BF_4)$ must be carried out in the minimum possible solvent. On adding excess trityl tetrafluoroborate as a solid to a highly concentrated dichloromethane solution of compound **21** at room temperature, an orange precipitate is observed after twenty minutes. The orange product has not been fully characterised but has been formulated as $[Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^5{-}C_6H_7)]^+$**25.**

The Infra red spectrum of compound **25** displays an absorption band pattern in the CO stretching region similar to that of the starting material $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2$

$-C_6H_6)(\eta^4-C_6H_8)$**21**, *albeit* shifted by 35-45 cm^{-1} to higher wavenumbers. This is indicative of a positively charged species. The mass spectrum although not conclusive displays a signal at 923amu (calc:-924), although the fragmentation pattern makes interpretation difficult. Abstraction of a hydride from the diene ligand would result in the formation of a cyclohexadienyl moeity. This dienyl group can either bind in an μ_3-face capping or an η^5-terminal mode. When the benzene-diene cluster $Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_2-C_6H_8)$**11** is reacted with trityl tetrafluoroborate the resulting cationic benzene-dienyl $[Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_3-\eta^2:\eta^2:\eta^1:-C_6H_7)]^+$ displays the dienyl in a face capping coordination . The is attributed to the nature of the diene precursor i.e. a bridging $\mu_2:\eta^2:\eta^2-C_6H_8$, therefore a μ_3- coordination would not require any carbonyl rearrangement at this stage. Applying this observation to compound **25** where the diene precursor is bound in an η^4- terminal mode, the resulting dienyl molecule would be expected to remain terminally bound to one osmium atom.

Deprotonation of compound **25** with the non-nucleophilic base 1,8- diazabicyclo [5.4.0] undeca-7-ene (DBU) results in the formation of one orange product. The product was initially characterised by spectroscopic techniques as $Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2-C_6H_6)(\eta^6-C_6H_6)$**24** . The mass spectrum exhibits a parent peak at 896amu(calc:-895) followed by the sequential loss of six carbonyl groups. The ^1H nmr spectrum is relatively simple displaying only two singlet resonances at δ5.42 and δ3.97 ppm. This indicates that in solution the two benzene ligands adopt differing coordination modes, one being terminally bound to a single osmium atom the other triply capping the triosmium face.

The molecular structure of compound **24** has been established and is shown together with some relevant bond lengths in Figure 3.9. Crystals suitable for X-ray analysis were obtained from a toluene solution at -30°C. The molecular structure of **24** consists of a regular triangular arrangement of osmium atoms with metal-metal bond lengths of 2.806, 2.841 and 2.843Å. Two benzene ligands are coordinated to the cluster, one in an η^6 manner, the other in a face capping $\mu_3:\eta^2:\eta^2:\eta^2$ fashion. In the former instance where the arene is terminally coordinated, the Os-C bond lengths range from 2.19 to 2.25Å. A wider variation of Os-C bond lenths are observed for the facially coordinated ligand where the bond lengths range from 2.14 to 2.36Å.

It is interesting to note that the facially bound benzene forms significantly shorter interactions with Os(3){mean Os-C_{facial} 2.18Å}, than it does to the two remaining osmium atoms {mean Os(1,2)-C_{facial} 2.33Å}. This effect has been observed previously

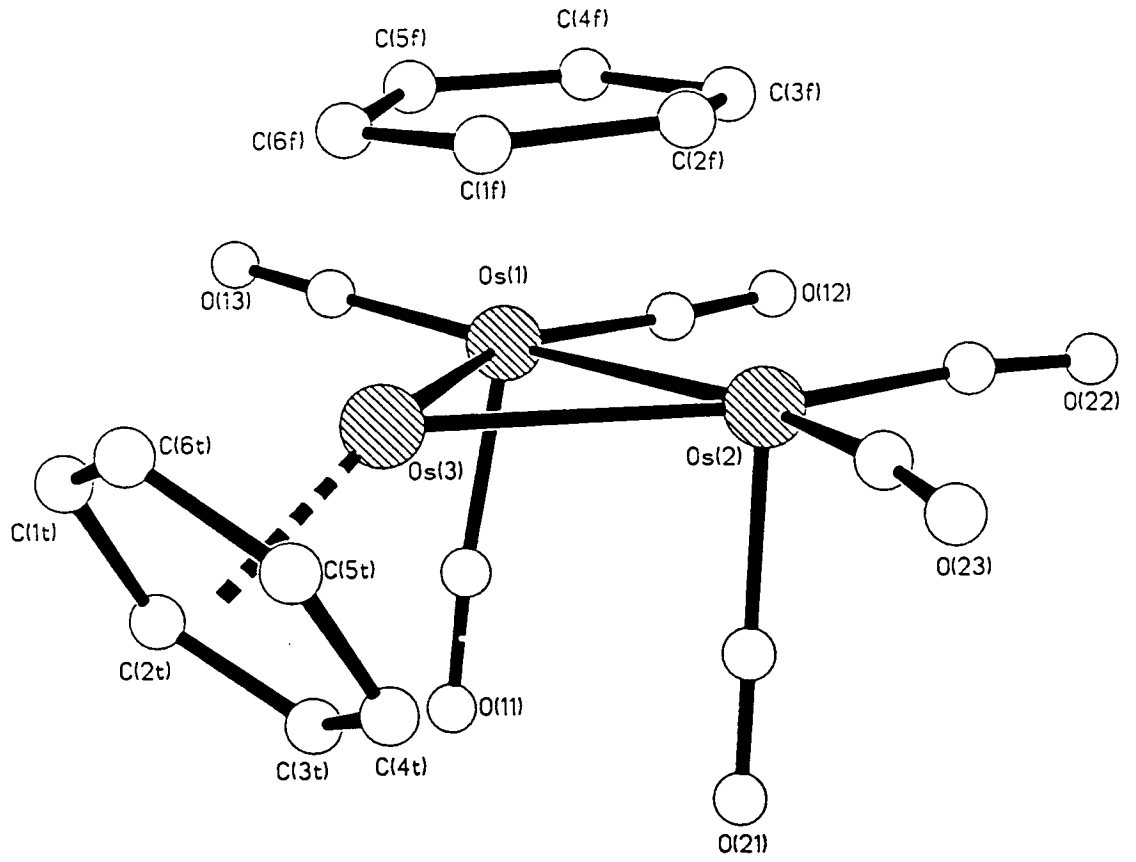


Figure 3.9: The solid state molecular structure of $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å): Os(1)-Os(2) 2.8414(13), Os(1)-Os(3) 2.8427(14), Os(2)-Os(3) 2.8059(14), Os(1)-C(4f) 2.28(2), Os(1)-C(5f) 2.36(2), Os(2)-C(3f) 2.32(3), Os(2)-C(2f) 2.34(2), Os(3)-C(6f) 2.14(2), Os(3)-C(1f) 2.21(2), Os(3)-C(1t) 2.22(3), Os(3)-C(2t) 2.23(3), Os(3)-C(3t) 2.20(2), Os(3)-C(4t) 2.25(3), Os(3)-C(5t) 2.20(2), Os(3)-C(6t) 2.19(2), C(1t)-C(6t) 1.30(3), C(1t)-C(2t) 1.44(4), C(2t)-C(3t) 1.41(3), C(3t)-C(4t) 1.39(3), C(4t)-C(5t) 1.41(3), C(5t)-C(6t) 1.40(3), C(1f)-C(6f) 1.41(3), C(1f)-C(2f) 1.45(3), C(2f)-C(3f) 1.38(3), C(3f)-C(4f) 1.49(3), C(4f)-C(5f) 1.40(3), C(5f)-C(6f) 1.40(3), mean Os-C (CO) 1.89(3), mean C-O 1.15(2).

in section 3.2 for the compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** , although in this case the effect is more prenounced. This asymmetry in coordination is probably due to the π -acceptor capability of the remaining ligands to which the metals coordinate. Both Os(1) and Os(2) have three terminally coordinated carbonyl ligands, whereas Os(3) is coordinated to the terminal benzene. The latter ligand has a greatly reduced π-acceptor capability as compared with that of the carbonyl groups and as a result there is more residual electron density available on Os(3) for back donation into

the π^* orbitals of the facially coordinated arene. Hence the average metal-C distance for Os(3){2.21Å} is significantly shorter than that for Os(1,2) {2.33Å}.

3.5 The molecular organisation of $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$24

The understanding of the crystal packing of molecules has increased in recent years. However, the nature of the intermolecular forces is far from being understood. Arene clusters due to the fact they possess both flat arene groups and cylindrical carbonyl ligands are well suited to investigating the relationship between molecular and crystal structure. The specific requirements of these two groupings pose problems for the optimisation of the intermolecular interlocking that controls crystals cohesion and stability.

The packing in crystalline arene clusters is largely governed by the need to maximise the intermixing of the arene fragments and protruding CO groups. This is achieved in *mono*-arene clusters by the formation of arene ribbons or layers through the crystal lattice. In the tetraosmium species $[H_2Os_4(CO)_{10}(\eta^6\text{-arene})]$ (arene = C_6H_6, C_6H_5Me & $C_6H_4Me_2$), a 'herring-bone' type orientation is produced by the interlocking of two rows of arene fragments in a 'chevron-like' fashion.[22] This packing motif has been observed previously in the mononuclear complex $Cr(C_6H_6)_2$[23] and is similar to that reported for crystals of condensed arenes such as naphthalene, anthracene and even benzene itself. In *bis*-arene clusters, packing optimisation is obtained by the formation of molecular rods or snakes, where the arene ligands face each other in a graphitic type arrangement. The *bis*-benzene molecule $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$[24] contains two benzene ligands occupying different bonding modes, one terminal the other face-capping. The interaction of the reference molecule and the two next nearest neighbours involves the pairing of the benzene ligands, in the sequence $\eta^6\eta^6\text{-}\mu_3\mu_3\text{-}\eta^6\eta^6$ etc. The benzene rings are not exactly superimposed, but are shifted in a typical graphitic pattern.

A similar packing motif is observed for the compound $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** and is depicted in Figure 3.10. The molecules pack in such a way that the terminal benzene ligand of one cluster lies above the facially bound arene of the adjacent molecule. The ligands are staggered with respect to each other, with an angle of 2.9° between the C_6 planes. The inter-ring separation is 3.39Å, displaying a typical graphitic interaction throughout the crystal lattice producing 'snake-like' chains. In the hexaruthenium *bis*-benzene cluster $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{:-}C_6H_6)$, the molecules are orientated such that terminal-terminal and facial-facial interactions are

observed. However, in compound **24** all interactions are of the type terminal-facial. This anomaly must occur to maintain optimum CO--CO interlocking in the remaining part of the molecule.

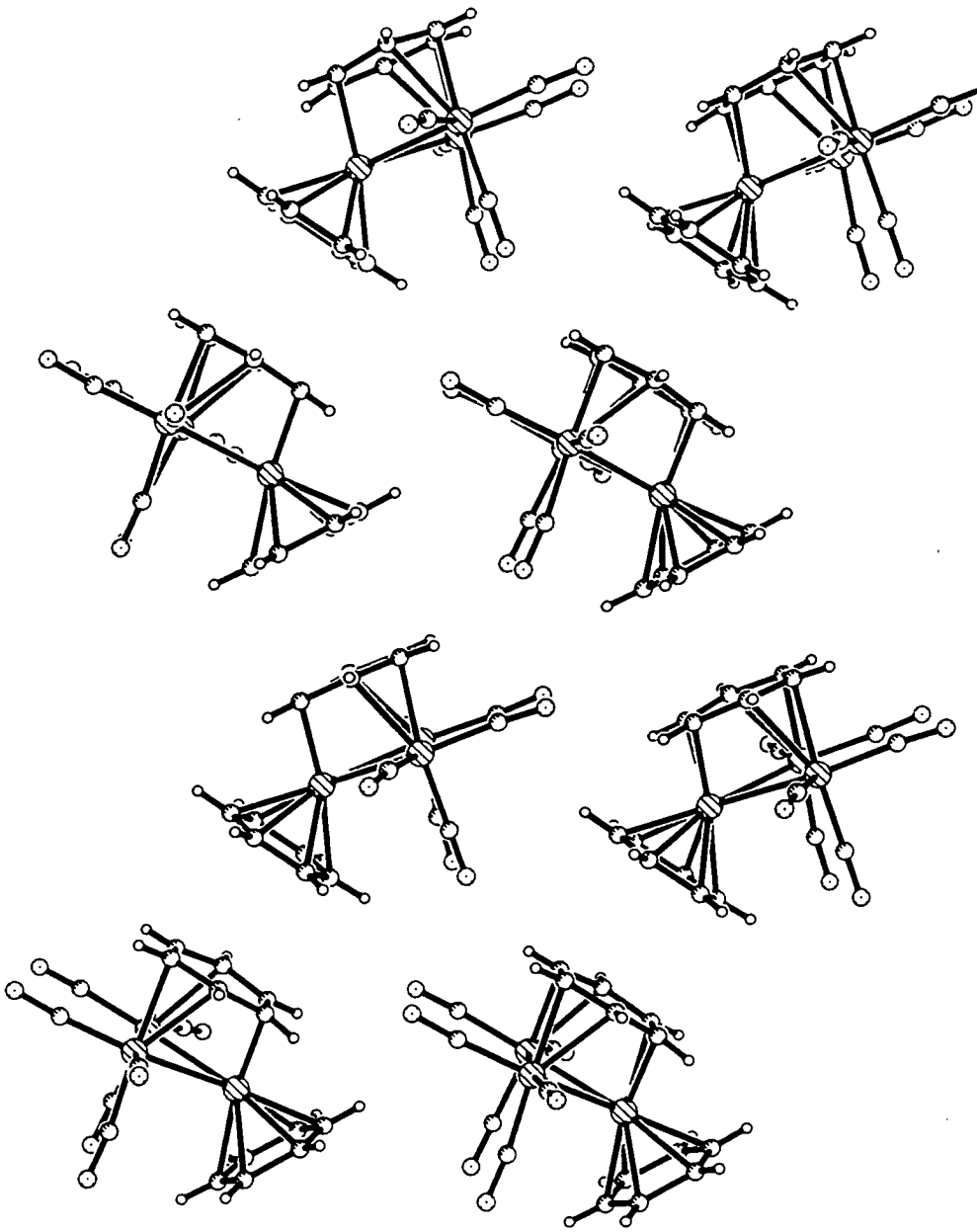


Figure 3.10: The molecular organisation of $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^6{-}C_6H_6)$**24**

3.6 Reaction of $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$23 with Me_3NO

In an attempt to synthesise the compound $H_2Os_3(CO)_6(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^6\text{-}C_6H_6)$, the compound $H_2Os_3(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** was treated with an equimolar quantity of Me_3NO in dichloromethane at -78°C. It was envisaged that removal of a CO ligand would generate a vacant coordination site on the cluster causing spontaneous C-H bond cleavage in the coordinated diene to form a terminally bound benzene. The reaction was monitored by IR spectroscopy and complete consumption of the starting material was achieved after one hour, a colour change from yellow to orange was also observed. Extraction of the products by tlc eluting with dichloromethane/hexane (4:6 v/v) mixture results in the isolation of one major orange product. The mass spectrum exhibits a parent peak at 957amu, followed by the sequential loss of six carbonyl groups. This does not agree with the formulation $H_2Os_3(CO)_6(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^6\text{-}C_6H_6)$ which would display a parent peak at 894amu. The ^1H nmr spectrum in CD_2Cl_2 is reminiscent of the spectrum obtained for compound **23**. Two hydride signals are observed at δ-17.46 and -15.10ppm, each showing a relative integral of one proton. The four signals at δ7.43, 7.15, 6.78 and 6.65ppm may be attributed to the benzyne unit on the basis of multiplicity and chemical shift. The series of signals in the region δ4.92-0.68ppm displaying a total relative intensity of eight protons are indicative of a coordinated cyclohexadiene moeity. However, a large singlet at δ3.06ppm displaying a relative integral of nine protons, suggests the compound contains a trimethyl amine ligand. This has been confirmed by elemental analysis and the compound formulated as $H_2Os_3(CO)_6(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$**26**.

The molecular structure of compound **26** has been established and is shown in Figure 3.11, together with some relevant bond lengths. Crystals suitable for X-ray analysis were grown from a toluene solution at -30°C. The solid state structure is reminiscent of compound **23**. The osmium atoms define an irregular triangle with metal-metal bond lengths of 3.06, 2.88 and 2.76Å. The C_6H_4 fragment continues to donate four electrons to the cluster forming two σ bonds with Os(1) and Os(2) and a π-interaction with Os(3), to which it is inclined at an angle of 68°. The cyclohexadiene ligand remains η^4-bound to Os(3) occupying two equatorial bonding sites. An axial carbonyl group on Os(1) has been replaced by a trimethylamine group displaying a Os-N bond length of 2.30Å. The six carbonyl ligands are terminally bound, three to Os(2), two equatorially to Os(1) and one occupying an axial site on Os(3). The hydride ligands

have not been located, due to the poor quality data obtained it proved impossible to ascertain their position conclusively.

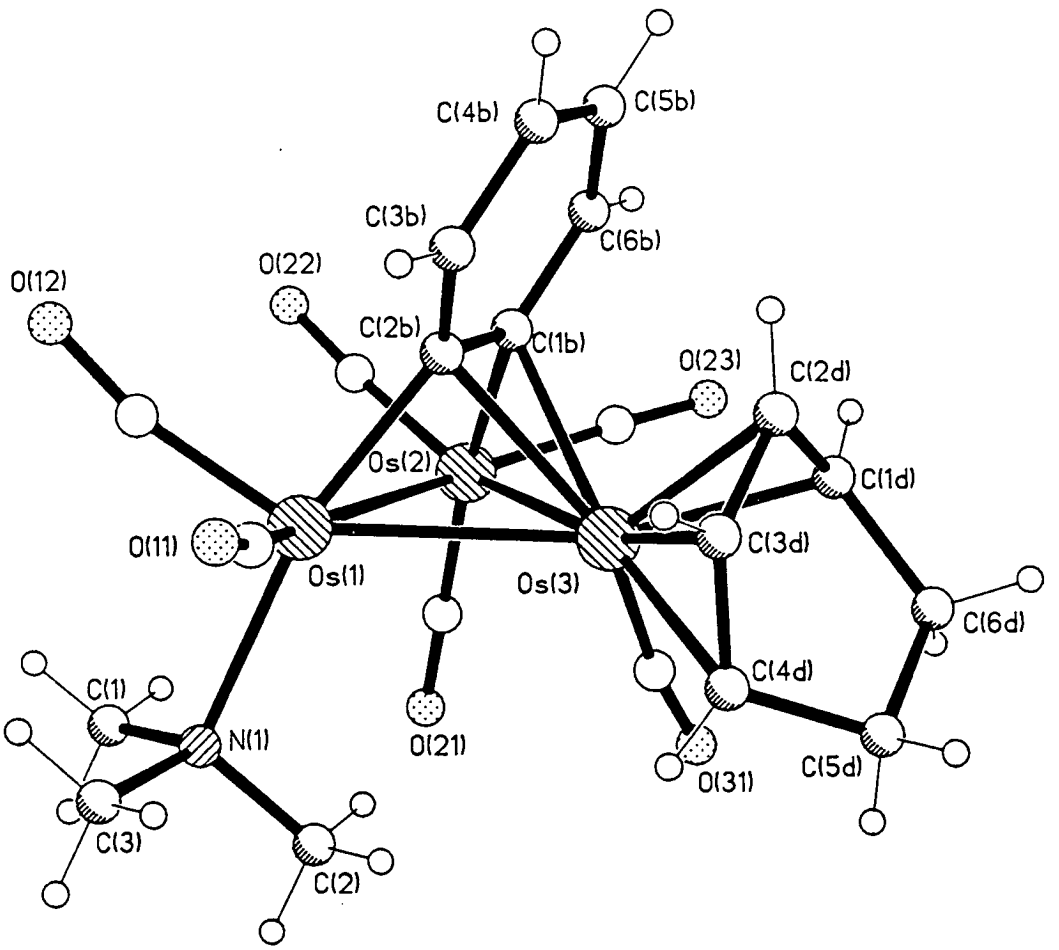


Figure 3.11: The solid state molecular structure of $H_2Os_3(CO)_6(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$ **26** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å): Os(1)-Os(2) 3.058(3), Os(1)-Os(3) 2.878(3), Os(2)-Os(3) 2.765(3), Os(1)-C(2b) 2.091(27), Os(2)-C(1b) 2.138(23), Os(3)-C(2b) 2.358(33), Os(3)-C(1b) 2.315(35), Os(3)-C(1d) 2.200(46), Os(3)-C(2d) 2.166(49), Os(3)-C(3d) 2.130(42), Os(3)-C(4d) 2.172(40), N(1)-Os(1) 2.302(42), N(1)-C(3) 1.508(54), N(1)-C(2) 1.483(58), N(1)-C(1) 1.441(55), C(1d)-C(6d) 1.540(64), C(1d)-C(2d) 1.458(59), C(2d)-C(3d) 1.488(60), C(3d)-C(4d) 1.465(54), C(4d)-C(5d) 1.572(67), C(5d)-C(6d) 1.572(71), benzyne C-C fixed 1.390, mean Os-C(CO) 1.84(3), mean C-O 1.19(3).

One of the most effective methods for initiating ligand substitution reactions in metal carbonyl clusters, under relatively mild conditions has been the use of trimethylamine-N-oxide. The success of this method relies on the ability of the reagent to create a vacant cordination site by oxidation of carbon monoxide to carbon dioxide. The trimethylamine group has a low coordination ability due to the high steric restrains of the amine. The coordination of a trimethylamine group to transition metal carbonyl cluster is extremely rare and has been observed previously in only one triosmium cluster $Os_3(CO)_9(NO)_2(NMe_3)$[25]. The long Os-N bond of 2.30Å reflects the good leaving-group potential of this ligand. However, when the compound **26** is heated in dichloromethane under reflux for 2 hours, major cluster decomposition occurs. Extraction of the products by tlc eluting with dichloromethane/hexane (3:7 v/v) as eluents leads to the recovery of $H_2Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$**26**, starting material, and a small amount of $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23**, presumably formed due to carbonyl scavenging.

3.7 Reaction of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ 4 with substituted dienes

3.7.1 *ortho* - 1,3 $Me_2C_6H_6$

The compound $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$**4** may be directly activated towards reaction with *ortho*-1,3 $Me_2C_6H_6$ upon treatment with an excess quantity of trimethyl amine N-oxide in dichloromethane. This reaction yields one major product which has been characterised on the basis of spectroscopic data as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}o\text{-}Me_2C_6H_6)$**27**. The mass spectrum exhibits a parent peak at 981 amu (calc:-980) followed by the consecutive loss of eight carbonyl groups. Verification of the benzene-diene complex **27** was based on the comparison of the infrared spectrum with that of the previously prepared benzene-η^2-diene compound $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20**. The IR spectrum in the CO stretching region was in good agreement and the cyclohexadiene moiety can be thought to bind in an η^2-fashion as a monoene. No evidence for an η^4-bound diene complex similar to compound **22**, where the diene moiety occupies two equatorial co-ordination sites has been observed in this case.

In an attempt to remove a further carbonyl group and ligate the cyclohexadiene moiety in an η^4-fashion, the compound $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}o\text{-}Me_2C_6H_6)$**27** was heated to 40°C with one molar equivalent of Me_3NO for three hours. Extraction of the products by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture resulted in the recovery of the starting compound **27** and major cluster

decomposition. No evidence for a compound of the type $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-diene})$ has been observed.

Using the computer simulation, previously mentioned in chapter two, the predicted molecular structures of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}o\text{-}Me_2C_6H_6)$ are depicted in Figure 3.12, together with a list of the closest bond contacts. Although this method is by no means accurate, it provides an indication of the steric interactions that may be encountered by the cyclohexadiene moiety, which may explain why the compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}o\text{-}Me_2C_6H_6)$ cannot be synthesised.

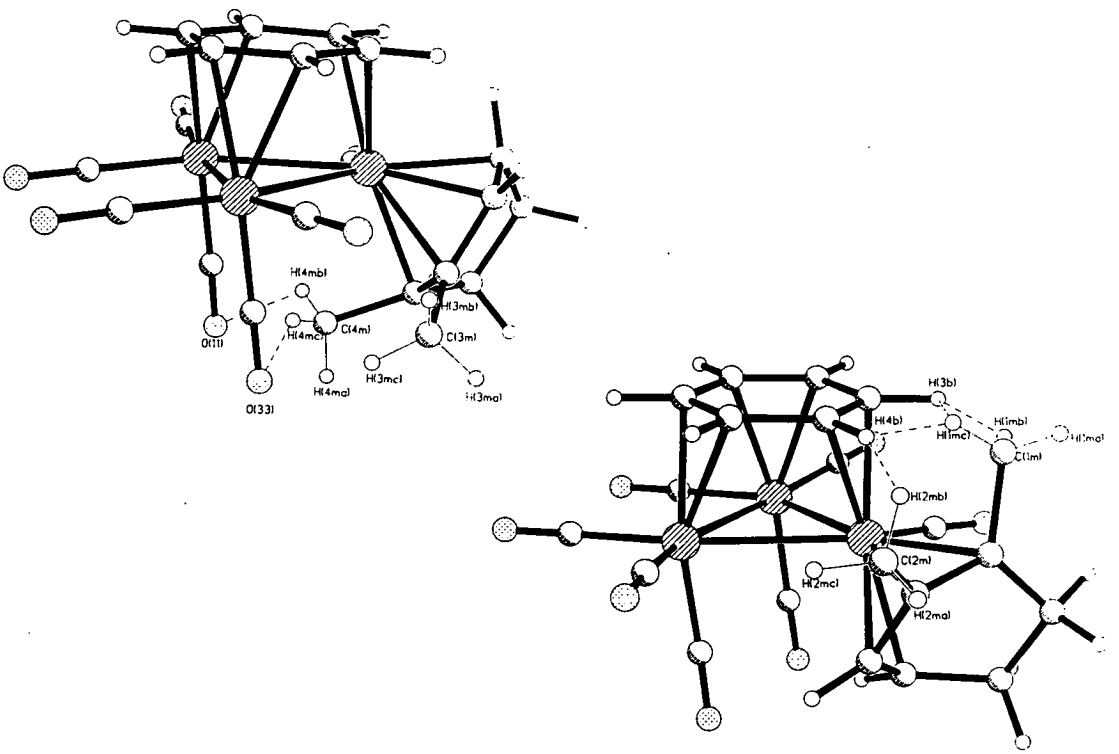


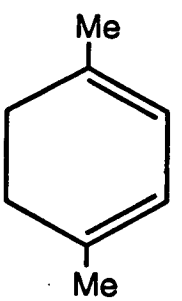
Figure 3.12: Predicted molecular structures of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}o\text{-}Me_2C_6H_6)$: Closest bond contacts (Å):- H(1mb)-H(3b) 1.25, H(1mc)-H(3b) 1.80, H(1mc)-H(4b) 1.35, H(2mb)-H(4b) 1.763, H(4mc)-O(11) 1.61, H(4mb)-O(33) 1.52

As can be shown from the values listed above a methyl group in the 1-position of the cyclohexadiene ring interacts strongly with the protons of the benzene ring, forming short contacts in the range of 1.3Å. Alternatively, a methyl group in the 4-position of the cyclohexadiene moiety interacts strongly with the adjacent axial carbonyl groups. These observations although tentatively proposed may provide an explanation for the inability to synthesise $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}o\text{-}Me_2C_6H_6)$

3.7.2 *para*-$Me_2C_6H_6$

Treatment of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)$**4** with *para*-1,3 $Me_2C_6H_6$ as described above, leads to the formation of two products. The first compound can be characterised as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}p{-}Me_2C_6H_6)$ **28** by the comparison of the IR spectrum with those previously obtained. The mass spectrum of compound **28** exhibits a parent peak at 982 amu (calc:-980) followed by the sequential loss of eight carbonyl groups. The second product has been characterised as $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}p{-}Me_2C_6H_6)$**29**, where the cyclohexadiene moiety occupies one axial and one equatorial bonding site. Again a comparison of the IR spectrum with the similar compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21**, appears to be in good agreement in the CO stretching region. The mass spectrum of compound **29** exhibits a parent peak at 954 amu (calc:-952).

The *para*- 1,3 $Me_2C_6H_6$ ligand used in the above reaction contained a mixture of two isomers depicted in Figure 3.13. In the major isomer the methyl groups occupy the 1,4-positions. As has been previously demonstrated above, methyl groups at these positions may result in unfavourable interactions with the protons of the benzene ring or adjacent carbonyl groups. It would therefore, appear likely that the minor isomer has co-ordinated. Unfortunately, due to time constraints, sufficient sample of compound **29** could not be obtained to record a ^1H nmr spectrum and confirm the predicted co-ordination.



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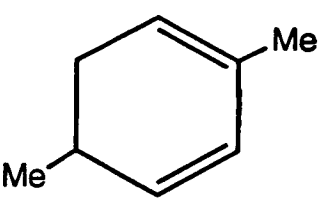

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Figure 3.13: Isomers of *para*- 1,3 $Me_2C_6H_6$

3.8 Concluding remarks

At the onset of this work, the primary objective was the synthesis of the *bis*-benzene sandwich cluster $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2\text{-}C_6H_6)_2$, where the two benzene moieties are facially bound, one above the Os_3 plane, the other below. A 'step-wise' synthetic approach was undertaken in an attempt to achieve this aim, uncovering a range of benzene-diene clusters. These compounds have proven themselves to be of some interest, undergoing a range of isomerisation reactions and fluxional behaviour. The photolytic conversion of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**2 1** to $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** has provided another example of C-H bond cleavage, where the analogy may be drawn to the interconversion of the associatively and dissociatively chemisorbed states of benzene on a metal surface.

The synthesis of a *bis*-benzene cluster has been successfully achieved. The compound $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** contains two benzene ligands, one capping the triosmium face, while the other is terminally bound to a single osmium atom. Attempts to convert compound **24** to the *bis*-benzene sandwich cluster have failed. This observation may be rationalised by considering the difficulty associated with the removal of axial carbonyl groups. The carbonyls *trans* to the facial benzene ring will demonstrate enhanced π-back bonding and as a result prove more difficult to substitute than the equatorial carbonyl ligands. An interesting feature of the *bis*-benzene cluster $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** is the molecular organisation in the solid state. The compound demonstrates a typical 'graphitic' interaction throughout the lattice producing 'snake-like' chains. This again demonstrates the need to optimise the intermixing of arene fragments and protruding CO groups in the crystalline packing of arene clusters.

The preparation of benzene-substituted diene complexes, although, only in it's infancy, should provide a wide range of information when fully developed. Hopefully the successful synthesis of mixed-arene triosmium cluster may in time be realised.

3.9 References

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CHAPTER 4:- Acenaphthylene Cluster Complexes

The interactions of arene with transition metal cluster complexes continues to stimulate ongoing research. However, studies are now being extended to a wider and more diverse range of cyclic and polycyclic systems. This chapter commences with an introduction to acenaphthylene co-ordination in transition metal carbonyl clusters. Acenaphthylene, $C_{12}H_8$, is a stable tricyclic system with 12 π–electrons available for bonding. The reactions of acenaphthylene with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are reported, demonstrating the wide range of bonding modes adopted by this flexible polycyclic ligand.

4.1 Introduction

4.1.1 Cluster Complexes of other Face-capping Carbocycles

Benzene and it's derivatives have been shown in previous chapters to be extremely versatile ligands, capable of adopting a wide variety of bonding modes. However their ability to span a triangulo-metal face is not unique. Isoelectronic 6π electron systems such as $(C_5H_5)^-$ and $(C_7H_7)^+$ have been reported to adopt a face-capping co-ordination in an number of transition metal complexes. A crystallographic study of the compounds $HRh_3(\eta^5C_5H_5)_3(\mu_3\text{-}C_5H_5)$[1] and $Ru_3(CO)_6(\mu_3\text{-}S^tBu)(\mu_3\text{-}C_7H_7)$ [2] reveal a planar bond delocalised co-ordination of the ligands in a face-capping manner.

Studies involving cyclooctatetraene (COT) have demonstrated the ability of a C_8-moiety to bond in a μ_3-fashion. In the complex $Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}C_8H_8)$[3], the C8 ligand spans the metal triangle and is is π-bonded through three double bonds to the cluster core, the fourth double bond having essentially no interaction with the cluster. In this case the ligand adopts a *tub* conformation and a distinct 'long-short-long' bond alternation is observed. In contrast, in the complex $Ni_3(CO)_3(\mu_3\text{:}\eta^2\text{-}CF_3C_2CF_3)(\mu_3\text{-}C_8H_8)$[4,5], the COT is virtually coplanar with the metal triangle and all eight carbons of the ring are involved in a highly delocalised co-ordination.

4.1.2 Co-ordination modes for Acenaphthylene in Transition Metal Complexes.

Acenaphthylene is a stable tricyclic hydrocarbon with a 12 π-electron bonding capacity. Over the years it has proved to be a very versatile ligand capable of bonding in many different ways. A summary of the bonding modes is represented in Figure 4.1.

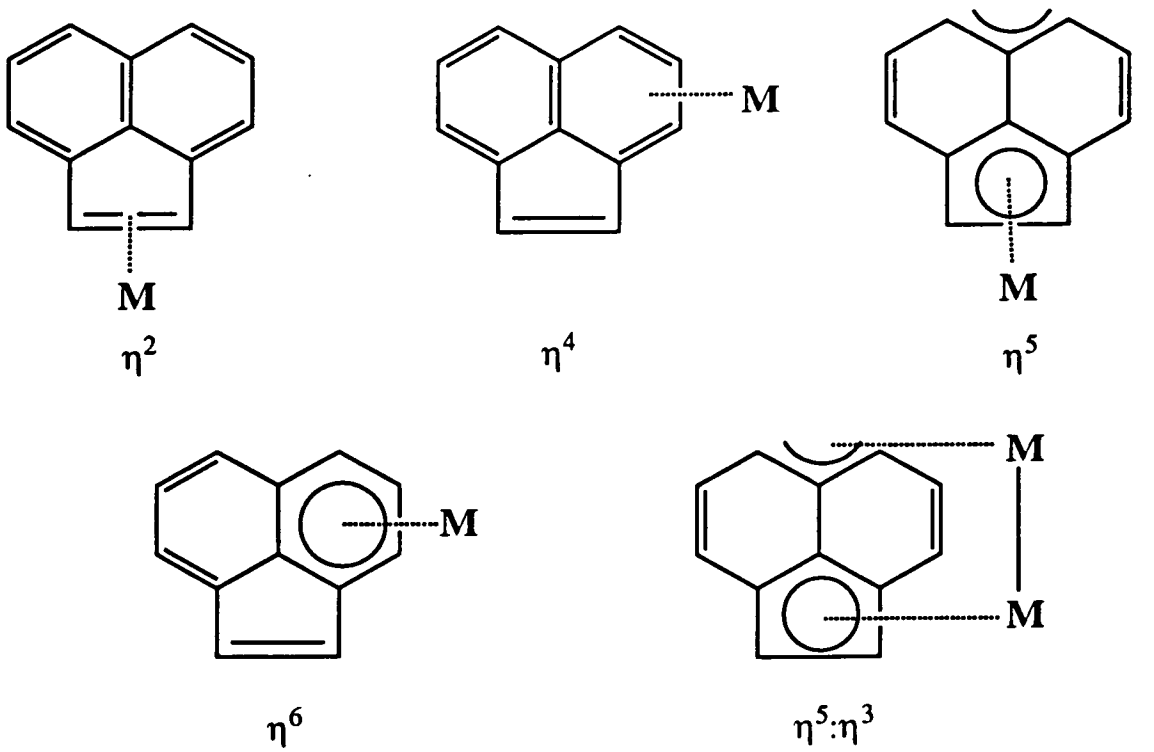

Figure 4.1: The co-ordination modes for acenaphthylene in transition metal complexes

η²and η⁴- Acenaphthylene Complexes

The η²-co-ordination mode for acenaphthylene has been reported in the compounds $CpCr(CO)(NO)(C_{12}H_8)$[6], $CpMn(CO)_2(C_{12}H_8)$[7] and $Fe(CO)_4(C_{12}H_8)$.[8] In all cases the acenaphthylene moiety is bound to the metal through the ethylenic carbons on the five membered ring. The compound $Fe(CO)_4(C_{12}H_8)$ can be easily prepared by the reaction of $Fe_2(CO)_9$ with acenaphthylene when heated under reflux in THF. Surprisingly, the molecular structure of $Fe(CO)_4(C_{12}H_8)$ proved to be the first accurate structure of the type (olefin)$Fe(CO)_4$.

An example of η⁴-co-ordination of the C_{12}-ligand is shown in Figure 4.2. In the complex $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$[9] the acenaphthylene has been hydrogenated and the resulting acenaphthene formly donates four electrons to the metal centre through two

double bonds within the six membered ring. In this case the planarity of the acenaphthylene has been lost and the complex adopts a pentagonal bipyramidal structure.

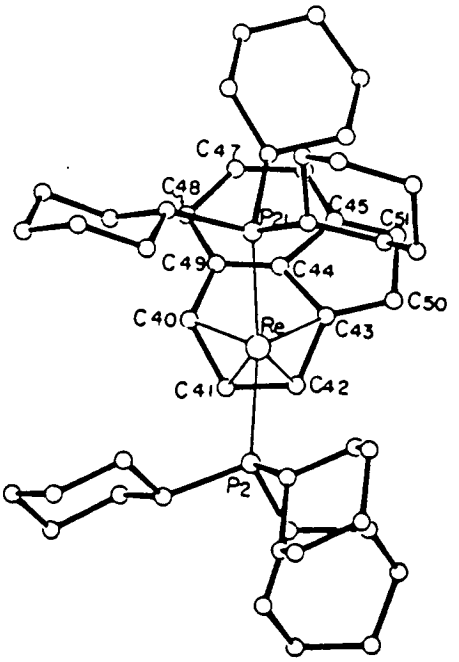

Figure 4.2: The molecular structure of $(\eta^4\text{-}C_{12}H_{10})ReH_3(PCy_3)_2$

<u>η^6-complexes</u>

η^6-arene ligands have been structurally characterised in a variety of mono- and poly-nuclear metal complexes.[10-13] For arene ligands, this is the most important and commonly observed co-ordination mode. However, for acenaphthylene there is apparently only one example which exhibits the η^6-bonding mode. The compound $(C_{12}H_8)Cr(CO)_3$[14] was first prepared by King and Stone in 1960. The $Cr(CO)_3$ group is bonded to one of the six membered rings in the acenaphthylene system enabling an 18 electron inert gas configuration to be acquired by the metal. Reactivity of the organic substrate is greatly modified upon co-ordination to the metal and subsequent studies[15] have involved the successful metallation, carbanion addition and free radical addition to the ligand.

<u>η^5-complexes</u>

Extensive crystallographic studies of azulene metal complexes such as $(C_{10}H_8)Fe_2(CO)_5$[16], $(C_{10}H_8)Mn_2(CO)_6$,[17] $[(CH_3)_3C_{10}H_5]Ru_4(CO)_9$[18] and $(C_{10}H_8)_2Fe_4(CO)_{10}$[19] have indicated that the dominant feature of azulene-metal

bonding is the utilisation of the five membered ring in a π-cyclopentadienyl-metal linkage. A similar interaction has been observed for acenaphthylene in the double half sandwich complex $[V(CO)_4(C_{12}H_8)]_2$.[20]

The *bis* η^5-co-ordination is obtained through the dimerisation of acenaphthylene as shown in Figure 4.3. The dimerisation of acenaphthylene can be achieved by irradiation with *ultraviolet* light to yield both *cis* and *trans* isomers, where the dimerisation has occured at the five membered ring.[21,22] However, in this case the dimerisation has occured at the six membered rings and can be rationalised by the production of radical intermediates in the reaction mechanism.

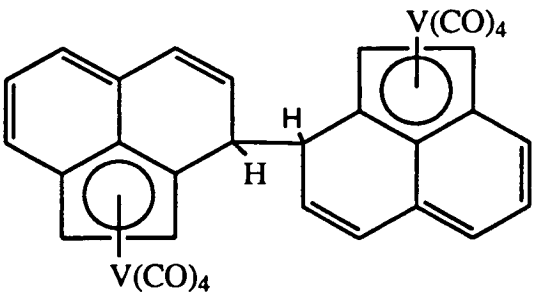

Figure 4.3: The double half sandwich complex $[V(CO)_4(C_{12}H_8)]_2$

Acenaphthylene as a bridging ligand

The ability of acenaphthylene to span two metal centres has been reported in the complex $(\mu_2:\eta^5:\eta^3\text{-}C_{12}H_8)Fe_2(CO)_5$.[23] A η^5-cyclopentadienyl interaction and an η^3-allylic co-ordination allow the $\mu_2\text{-}C_{12}H_8$ to formly donate eight of the twelve available electrons. As shown in Figure 4.4 the complex can exist as two separate isomers; both of which have been isolated. The symmetrical isomer I can undergo a haptotropic rearrangement on photolysis to produce the asymmetric isomer II.[24] The rearrangement is reversible and isomer II will slowly reform isomer I when protected from light.

A reversible change of co-ordination could substantially affect the physical properties of the metal complex. The migration of a metal group between two fused five or six membered rings has been reported previously for complexes containing naphthalene[25] and fluorenyl ligands.[26,27]

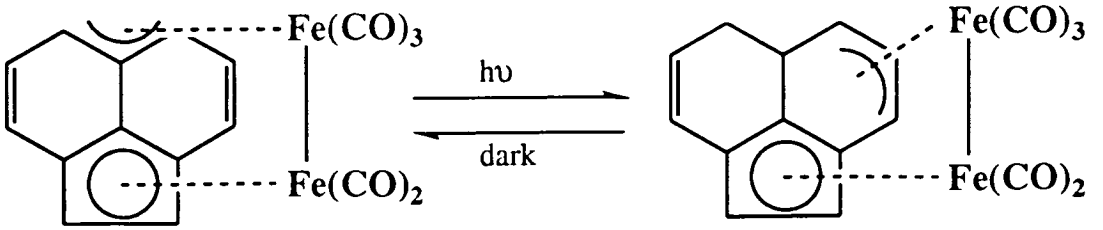

Figure 4.4: The haptotropic rearrangement of $(\mu_2{:}\eta^5{:}\eta^3\text{-}C_{12}H_8)Fe_2(CO)_5$

4.2 Preparation of $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2 - C_{12}H_8)$30

The thermolysis of $Ru_3(CO)_{12}$2 with an arene ligand has been shown to produce cluster build up to form $Ru_6C(CO)_{14}$(arene) clusters[28], where the arene moiety is terminally bound to one apical ruthenium atom. In the case of 2,2 paracyclophan, cluster build up is again observed however the preferred co-ordination appears to be the alternative μ_3-face capping mode.[29]

On heating a solution of $Ru_3(CO)_{12}$2 in octane under reflux with $C_{12}H_8$ a colour change is observed from orange to dark red after 4 hours. Isolation of one major product in approximately 80% yield is achieved chromatographically on silica eluting with dichloromethane/hexane (3:7 v/v). The product was initially formulated as $Ru_3(CO)_7(C_{12}H_8)$ **30** on the basis of the FAB mass spectrum. A parent peak at 651 amu (calc:- 651) was observed followed by the sequential loss of seven carbonyl groups. The ^1H nmr spectrum in CD_2Cl_2 exhibits eight distinct signals indicating the the acenaphthylene ligand is bound in an asymmetrical fashion.

In order to determine the co-ordination mode of the ligand to the cluster core, single crystals have been obtained from a dichloromethane solution at -30°C and X-ray analysis carried out. Two independent molecules were found in the asymmetric unit, both were chemically equivalent and the molecular structure of one of the molecules is shown in Figure 4.5 with some important bond lengths . The ruthenium atoms retain a triangular arrangement with metal-metal bond lengths of 2.75, 2.88 and 2.93Å.The significant shortening of the Ru(1)-Ru(2) bond can be accounted for by the presence of a bridging carbonyl ligand. The remaining six carbonyl groups are terminally

coordinated, two to each ruthenium atom. The triply-bridging acenaphthylene moiety lies over the Ru_3 face such that the dihedral angle between the plane of the C_{12} ligand and that of the metal triangle is 6.8°. This implies an almost parallel arrangement. However, closer examination reveals that the face capping co-ordination causes a small deviation from planarity in the organic ligand by 0.06Å. The five membered ring is bent 7.6° out of the plane defined by the two six membered rings and shows a larger dihedral angle of 11.6° to the *triangulo* unit.

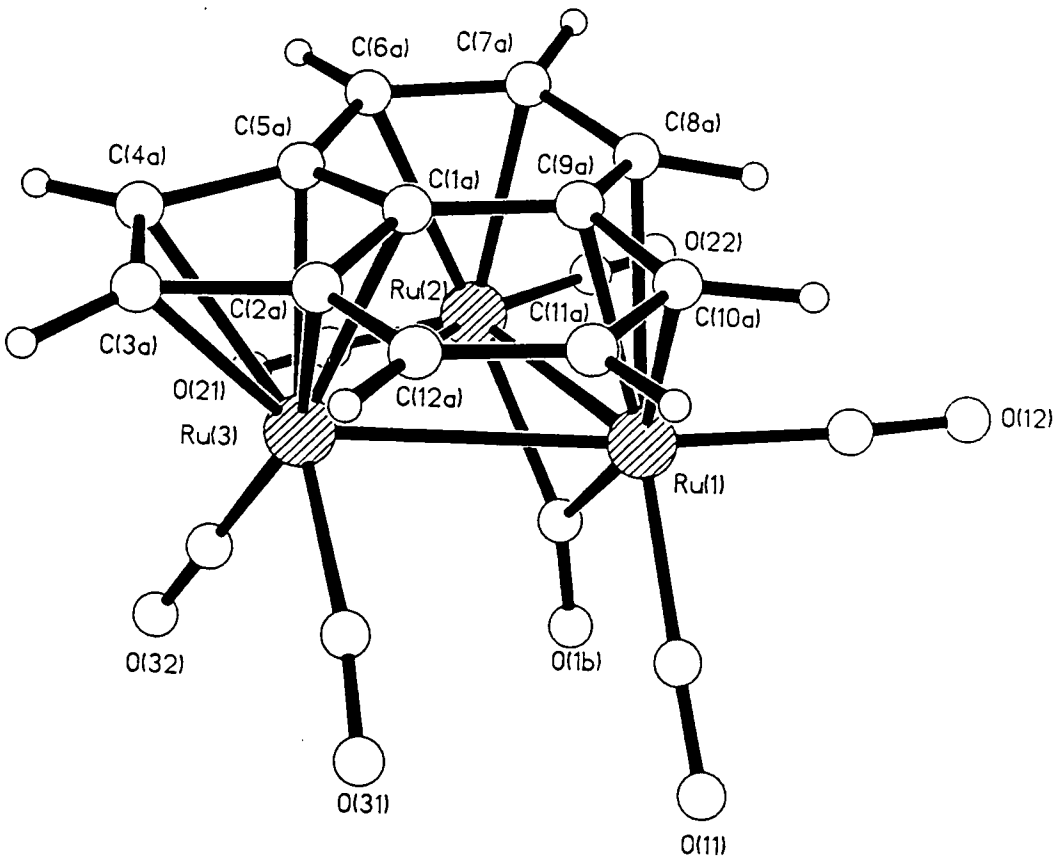

Figure 4.5: The solid state molecular structure of $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)30$ showing the appropriate atomic numbering scheme. The C atoms of the carbonyl groups bear the same number as the corresponding O atoms. Relevant bond lengths(Å):- Ru(1)-Ru(2) 2.7487, Ru(1)-Ru(3) 2.8757, Ru(2)-Ru(3) 2.9280, Ru(1)-C(1b) 2.1074, Ru(2)-C(1b) 2.0093, Ru(3)-C(1a) 2.2061, Ru(3)-C(2a) 2.2265, Ru(3)-C(3a) 2.2434, Ru(3)-C(4a) 2.2731, Ru(3)-C(5a) 2.2321, Ru(2)-C(6a) 2.3669, Ru(2)-C(7a) 2.2673, Ru(1)-C(8a) 2.4463 Ru(1)-C(9a) 2.2791, Ru(1)-C(10a) 2.4483, C(1a)-C(2a) 1.3902, C(1a)-C(5a) 1.4372, C(1a)-C(9a) 1.4021, C(2a)-C(3a) 1.4606, C(2a)-C(12a) 1.4630, C(3a)-C(4a) 1.4330, C(4a)-C(5a) 1.4057, C(5a)-C(6a) 1.4573, C(6a)-C(7a) 1.4030, C(7a)-C(8a) 1.4513, C(8a)-C(9a) 1.4387, C(9a)-C(10a) 1.4354, C(10a)-C(11a) 1.4071, C(11a)-C(12a) 1.3223, mean Ru-C(COterminal) 1.877, mean C-O(terminal 1.128)

All three ruthenium atoms are bonded directly to the acenaphthylene ligand, each atom exhibiting a different type of interaction. Thus, Ru(3) is involved in an η^5-cyclopentadienyl-metal linkage, Ru(2) an η^2-olefin and Ru(1) an η^3- allyl-metal interaction All interatomic distances are within the excepted range for normal interactions of these types. The ligand therefore formly donates ten electrons to the cluster core leading to the 48 electron system. The C-C bond lengths of the coordinated carbon atoms range from 1.39-1.46 Å where as the uncoordinated double bond is significantly shorter with a C-C bond length of 1.32Å. Metal-carbon bond lengths of 2.21-2.45Å are observed. In addition to the interaction of C(8) with Ru(1) (bond length 2.45Å) there appears to be a longer range interaction with Ru(2) (bond length 2.65Å).

As previously shown in 4.1.2 the η^5-cyclopentadienyl metal co-ordination is frequently found in azulene metal complexes. Perhaps the closest structural analogy to **30** is the triruthenium azulene compound $Ru_3(CO)_7(C_{10}H_8)$,[30,31] where five carbonyl groups have been replaced and the ligand bonds in a η^5-cyclopentadienyl and a η^5-dienyl fashion donating ten electrons to the cluster in total.

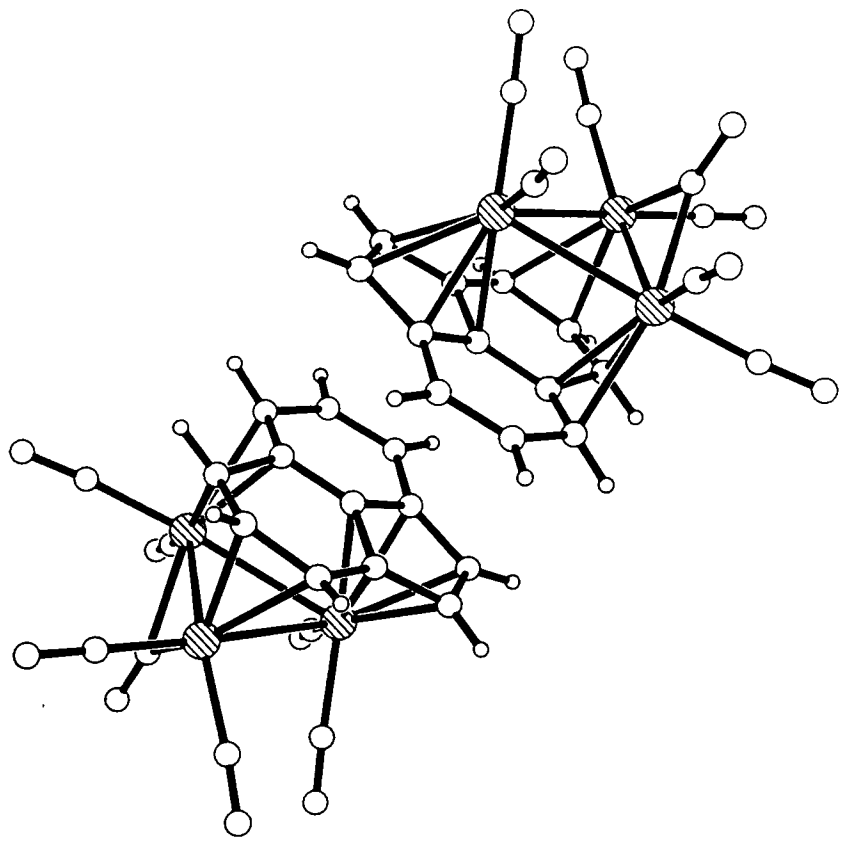

Figure 4.6: The molecular organisation of crystalline **30**

In the solid state, the molecular organisation of compound **30** involves the formation of *'dimers'* (Figure 4.6) where the two molecules are related through an inversion centre. The distance between the acenaphthylene planes is *ca* 3.4 Å and can be thought of as a 'graphitic type' interaction. As can be seen in Figure 4.6 the ring pairs are not exactly superimposed but are shifted in a typical graphitic pattern. This type of interaction is consistent with previous studies, [32,33] which have led to the suggestion that the interlocking of flat arenes and uneven carbonyls is not efficient and that intermolecular packing is optimised when arene-arene and CO-CO interactions occur.

The molecular structure of $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$**30** and a series of homonuclear decoupling/ nOe nmr experiments have led to the full assignment of the ^1H nmr spectrum. The acenaphthylene ligand displays eight distinct signals all of which have equal relative intensities, the chemical shift values can be seen in Table 4.1. The most intriguing feature of the ^1H nmr spectrum is the signal at δ2.60ppm; this is an extremely low frequency for such a proton, it does however support the interaction of C(8A) with the two ruthenium atoms Ru(1) and Ru(2). The $^{13}C\{^1H\}$ nmr spectrum exhibits twelve signals, again confirming the asymmetry of the bound ligand. The signals deriving from the quaternary carbons are found at δ 96.88, 86.50, 82.67 and 77.36ppm. Assignment of the eight proton bearing carbons has been carried out using a two-dimensional $^{13}C/^1H$ correlation experiment (Figure 4.7) and chemical shift values are displayed in Table 4.1.

C/H	$\delta\,^1H$	$\delta\,^{13}C$
8	2.60	35.5
4	4.94	79.3
10	5.51	65.1
7	5.60	66.2
12	5.81	114.0
3	6.03	76.1
11	6.22	128.3
6	6.50	63.2

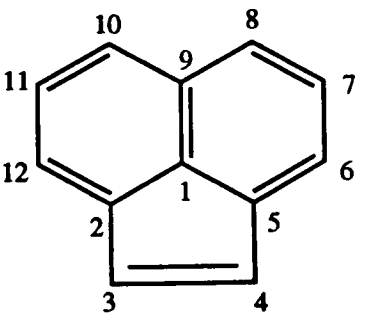

Table 4.1: The assignment of protons and carbons in $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$**30**

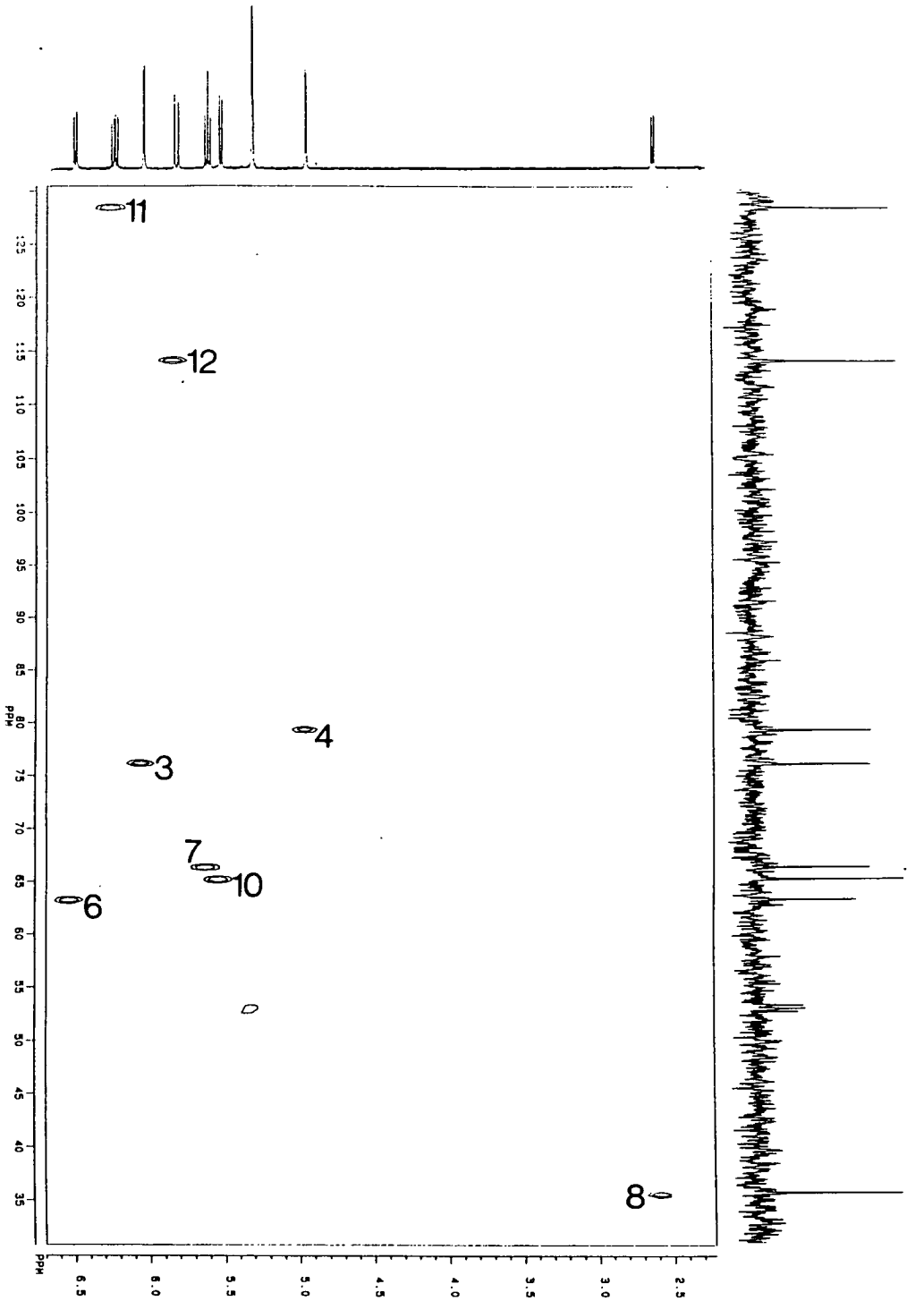

Figure 4.7: The $^{13}C/^{1}H$ correlation nmr spectrum for $Ru_3(CO)_7(\mu_3:\eta^5:\eta^3:\eta^2 - C_{12}H_8)$**30**

4.3 Reactivity of $Ru_3(CO)_7(\mu_3:\eta^5:\eta^3:\eta^2 - C_{12}H_8)$30

The reaction of a dichloromethane solution of $Ru_3(CO)_7(\mu_3:\eta^5:\eta^3:\eta^2\text{-}C_{12}H_8)$**30** with carbon monoxide gas at room temperature, displays a colour change from red to orange within 15 minutes. Extraction of the products by tlc, eluting with dichloromethane/hexane (4:6 v/v) results in the formation of an orange and a yellow band. The two products have been formulated as $Ru_3(CO)_{12}$**2** and $C_{12}H_8$ respectively. This result indicates the ease with which the ligand can be displaced from the cluster.

Acenaphthylene as a free ligand is extremely reactive at the ethylenic linkage on the five membered ring and can be easily converted to acenaphthene by catalytic hydrogenation.[34] The reaction with chlorine gas gives *cis* dichloroacenaphthene[35] where as the reaction with iodobenzene dichloride yields the *trans* isomer[36]. Acenaphthylene can also react with compounds such as benzyne or maleic anhydride to give *cyclobutano* derivatives.[37]

In the compound $Ru_3(CO)_7(\mu_3:\eta^5:\eta^3:\eta^2\text{-}C_{12}H_8)$**30**, the ligand has one uncoordinated double bond located on a six membered ring. It was proposed to carry out addition reactions targeting this double bond in an attempt to synthesise new acenaphthylene derivatives, which could be easily displaced from the cluster core by reaction with carbon monoxide. Unfortunately Nagashima *et al* reported the successful partial hydrogenation of acenaphthylene on the face of a triruthenium cluster forming $H_2Ru_3(CO)_7(\mu_2:\eta^5:\eta^1\text{-}C_{12}H_{10})$[38], therefore no further reactions with $Ru_3(CO)_7(\mu_3:\eta^5:\eta^3:\eta^2\text{-}C_{12}H_8)$**30** were investigated.

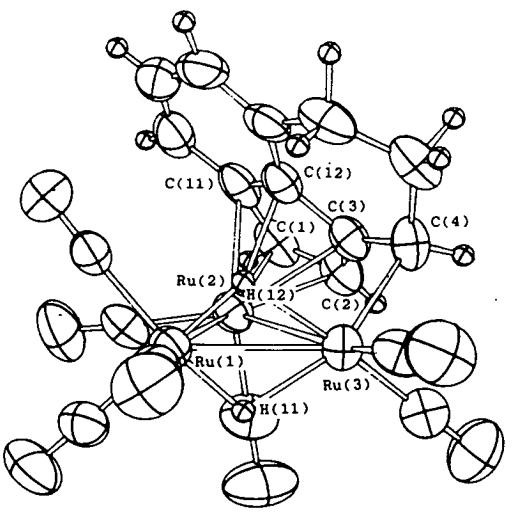

Figure 4.8: The molecular structure of $H_2Ru_3(CO)_7(\mu_2:\eta^5:\eta^1\text{-}C_{12}H_{10})$

Nagashima has shown that hydrogenation of compound **30** in dichloromethane at room temperature can be achieved in 9 hours under 1-8atm H_2 gas in approximately 70% yield. The compound has been fully characterised as $H_2Ru_3(CO)_7(\mu_2{:}\eta^5{:}\eta^1\text{-}C_{12}H_{10})$ and the molecular structure is shown in Figure 4.8. The dihydroacenaphthylene ligand is bonded to two ruthenium atoms in a μ_2-fulvene co-ordination mode. The successful hydrogenation has taken place within the six membered ring as expected. This dihydroacenaphthylene species has never before been isolated and it appears that the cluster has the ability to stabilise an otherwise unstable species.

4.4 Synthesis and characterisation of some osmium clusters containing acenaphthylene

The reaction of $Os_3(CO)_{10}(MeCN)_2$**3** with acenaphthylene heated in octane under reflux for 4 hours affords one major product, which may be isolated from the other minor products by tlc eluting with dichloromethane/ hexane (4:6 v/v) . The compound was initially formulated as $H_2Os_3(CO)_9(C_{12}H_6)$**31** on the basis of the IR spectrum. The spectrum is almost identical in the CO stretching region to $H_2Os_3(CO)_9(C_6H_4)$.[39,40] The mass spectrum exhibits a parent peak at 975 amu (calc:-973) followed by the sequential loss of nine carbonyl groups, which corroborates with the IR evidence. The ^1H nmr spectrum of compound **31** contains a broad resonance at δ -18.96ppm, typical of a hydride and two doublets at δ 7.86 and 7.82 and a multiplet at δ7.60 ppm with relative intensities 1:1:4. On cooling the sample to 223K the broad hydride resonance is resolved to two singlets at δ -16.59 and -20.55ppm.

The molecular structure of $H_2Os_3(CO)_9(C_{12}H_6)$**31** in the solid state has been established by single crystal X-ray analysis. Crystals suitable for analysis were obtained from a dichloromethane solution at 5°C. The molecular structure of **31** is depicted in Figure 4.9 together with some relevant bond lengths and angles. The osmium atoms define an irregular triangle with metal-metal bond lengths of 2.76, 2.87 and 3.08Å. The organic ligand has undergone C-H bond cleavage at the five membered ring and is bonding to the cluster in a benzyne fashion. The acenaphthylene moiety remains essentially planar, inclined at an angle of 66° to the osmium triangle. This $C_{12}H_6$ fragment serves as a four electron donor, forming two σ bonds with Os(3) and Os(2) and a π- interaction with Os(1). The nine carbonyl ligands are all terminally bound, three to each Os atom. Although the hydrides have not been located directly, through the distribution of the carbonyl ligands they maybe assumed to bridge the Os(2)-Os(3) and Os(1)-Os(3) edges.

The Os-Os-C(carbonyl) angles for the carbonyl groups adjacent to these edges are significantly wider (mean 102°) than for the carbonyls adjacent to the edge Os(1)-Os(2) (mean 95°). This widening of carbonyl angles can be attributed to the steric influence of the bridging hydrides.

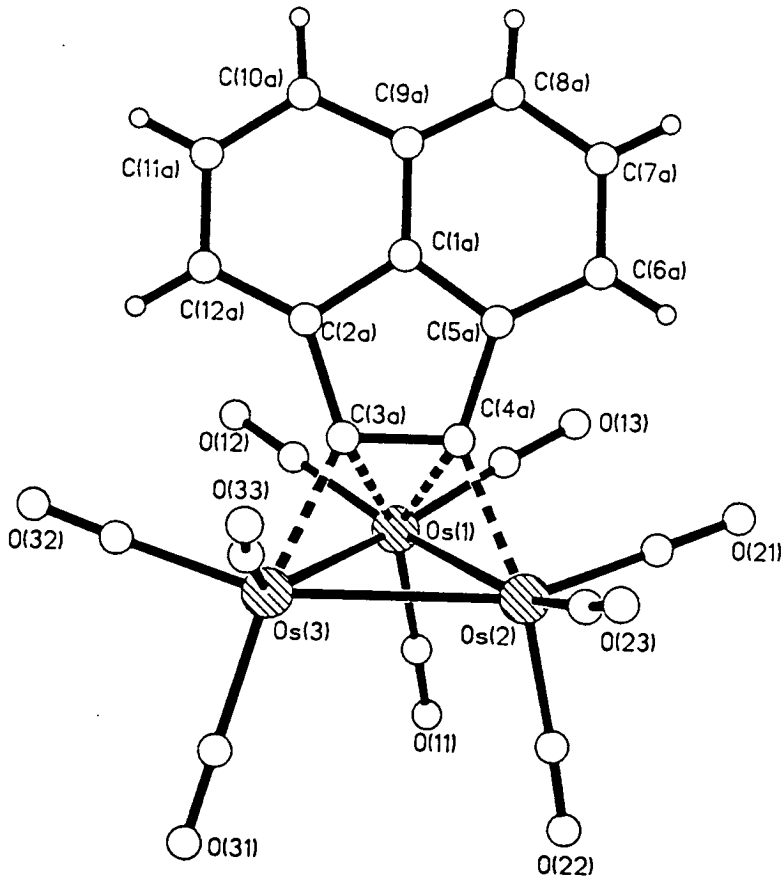

Figure 4.9: The solid-state molecular structure of $H_2Os_3(CO)_9(C_{12}H_6)$**31,** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å):- Os(1)-Os(2) 2.7631(13), Os(1)-Os(3) 2.8721(13), Os(2)-Os(3) 3.077(2), Os(1)-C(3a) 2.28(2), Os(1)-C(4a) 2.34(2), Os(2)-C(4a) 2.07(2), Os(3)-C(3a) 2.10(2), C(1a)-C(9a) 1.39(3), C(1a)-C(5a) 1.40(3), C(1a)-C(2a) 1.43(3), C(2a)-C(12a) 1.38(3), C(2a)-C(3a) 1.51(2), C(3a)-C(4a) 1.40(3), C(4a)-C(5a) 1.52(3), C(5a)-C(6a) 1.38(3), C(6a)-C(7a) 1.40(3), C(7a)-C(8a) 1.39(3), C(8a)-C(9a) 1.40(3), C(9a)-C(10a) 1.41(3), C(10a)-C(11a) 1.38(3), C(11a)-C(12a) 1.40(3), mean Os-C (CO) 1.92(2), mean C-O 1.14(2). Relevant bond angles(°):- C(13)-Os(1)-Os(2) 92.2(5), C(12)-Os(1)-Os(3) 101.9(6), C(3a)-Os(1)-Os(3) 46.5(4), Os(2)-Os(1)-Os(3) 66.17(3), C(21)-Os(2)-Os(1) 98.2(5), C(23)-Os(2)-Os(3) 104.0(6), C(4a)-Os(2)-Os(3) 66.6(5), Os(1)-Os(2)-Os(3) 58.62(2), C(32)-Os(3)-Os(1) 104.5(5), C(33)-Os(3)-Os(2) 98.4(6), C(3a)-Os(3)-Os(2) 65.9(5), Os(1)-Os(3)-Os(2) 55.22(3), Os(3)-C(3a)-Os(1) 81.9(6), Os(2)-C(4a)-Os(1) 77.3(6).

The cluster $Os_3(CO)_{12}$**1** when heated in nonane under reflux at 152°C with excess acenaphthylene affords a range of products in moderate yields. Separation of the products by tlc eluting with a dichloromethane/hexane mixture(2:8 v/v) results in the isolation of four major bands. In order of elution the first yellow band was characterised as $H_2Os_3(CO)_9(C_{12}H_6)$**31** by comparison with previously obtained spectroscopic data. The yield of $H_2Os_3(CO)_9(C_{12}H_6)$**31** is greatly reduced in this reaction compared to the method described previously and competing reactions must therefore be taking place. Confirmation of cluster build up was obtained by the characterisation of the fourth brown band as $Os_6(CO)_{18}$**32**. However, no evidence for ligand co-ordination to higher nuclearity clusters has been observed.

Crystals suitable for X-ray analysis were grown from a chloroform solution of compound **32** at -30°C. An initial examination of the crystals revealed the space group and unit cell dimensions to be contradictory to those previously published. The molecular structure of $Os_6(CO)_{18}$**32** was first determined in 1973 by Mason *et al* .[41] Initially it was suggested that the two different structures could be an example of organometallic crystal polymorphism. Previous studies on the prototypical hexa ruthenium carbidocarbonyl cluster $Ru_6C(CO)_{17}$[42] have revealed that the complex possesses three different molecular structures in the solid state. These structures differ essentially in the rotameric conformation of the tricarbonyl units above and below the equatorial plane containing bridging and semi-bridging ligands. The conformations being either eclipsed or staggered. However, closer examination of the structural data of $Os_6(CO)_{18}$ revealed the hexaosmium cluster to be solvated with chloroform. There appeared to be essentially no variations in the internal geometry when compared with the unsolvated molecule. The molecular structure consists of a bicapped tetrahedral Os_4 cluster, the bond parameters being consistent with those previously reported. However, significant O--H and O--Cl contacts with the chloroform solvate molecule are observed.

The second and third orange and yellow bands were initially formulated as $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** and $Os_2(CO)_6(C_{12}H_6)_2$**34** on the basis of spectroscopic information. The mass spectrum of compound **33** exhibits a parent peak at 1126 amu (calc:-1124) followed by the sequential loss of nine carbonyl groups. From this information it would appear that two acenaphthylene ligands have successfully co-ordinated to the cluster core. The ^1H nmr spectrum in CD_2Cl_2 displays a resonance at δ -18.08ppm, typical of a hydride and a series of signals from δ 8.70-4.20ppm, indicating unsymmetrical co-ordination of the two acenaphthylene ligands. In order to determine the co-ordination mode of the ligands, single crystals were obtained by slow

evaporation of a dichloromethane solution of compound **33** and single crystal X-ray analysis carried out. The solid state molecular structure is depicted in Figure 4.10 together with some relevant bond parameters.

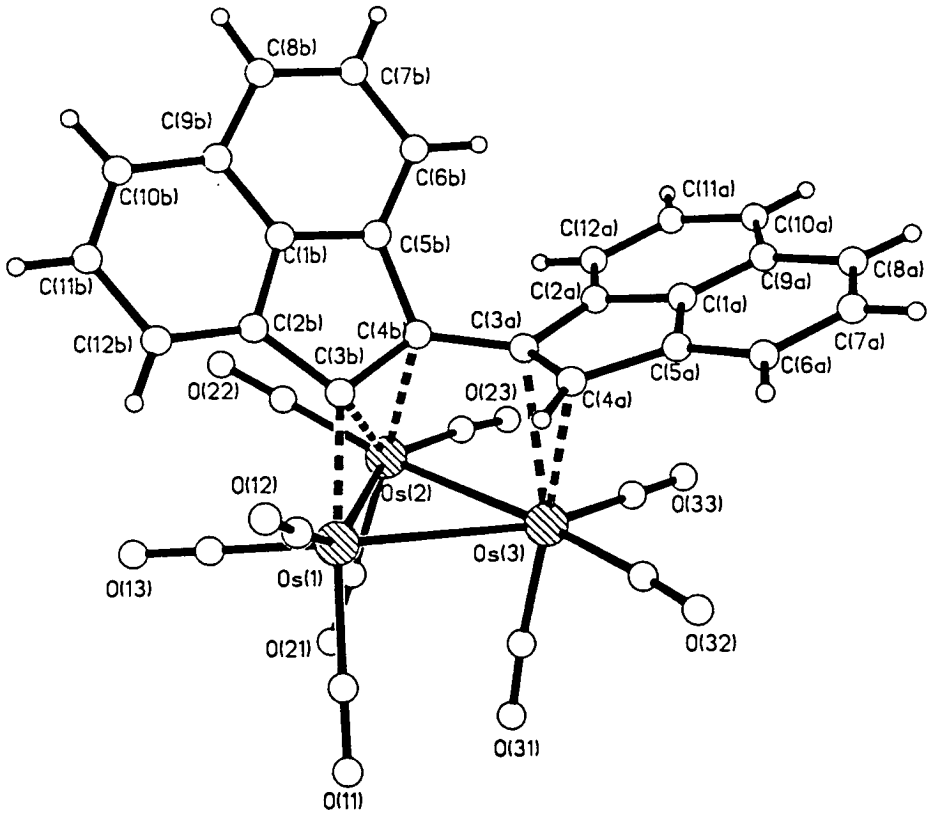

Figure 4.10: The solid-state molecular structure of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å):-Os(1)-Os(2) 2.759(3), Os(1)-Os(3) 2.979(3), Os(2)-Os(3) 2.899(4), Os(1)-C(3b) 2.088(10), Os(2)-C(3b) 2.287(9), Os(2)-C(4b) 2.320(10), Os(3)-C(4a) 2.342(10), Os(3)-C(3a) 2.464(10), C(1a)-C(9a) 1.38(2), C(1a)-C(5a) 1.398(14), C(1a)-C(2a) 1.410(14), C(2a)-C(12a) 1.382(14), C(2a)-C(3a) 1.48(2), C(3a)-C(4a) 1.421(14), C(3a)-C(4b) 1.49(2), C(4a)-C(5a) 1.50(2), C(5a)-C(6a) 1.386(14), C(6a)-C(7a) 1.41(2), C(7a)-C(8a) 1.36(2), C(8a)-C(9a) 1.45(2), C(9a)-C(10a) 1.42(2), C(10a)-C(11a) 1.38(2), C(11a)-C(12a) 1.39(2), C(3b)-C(4b) 1.44(2), C(3b)-C(2b) 1.48(2), C(4b)-C(5b) 1.53(2), C(5b)-C(6b) 1.39(2), C(5b)-C(1b) 1.40(2), C(6b)-C(7b) 1.41(2), C(2b)-C(12b) 1.38(2), C(2b)-C(1b) 1.411(14), C(12b)-C(11b) 1.43(2), C(11b)-C(10b) 1.36(2), C(10b)-C(9b) 1.40(2), C(9b)-C(1b) 1.38(2), C(9b)-C(8b) 1.40(2), C(7b)-C(8b) 1.37(2),. mean Os-C(CO) 1.91(1), mean C-O 1.15(1) . Relevant bond angles(°):- C(13)-Os(1)-Os(2) 85.8(3), C(3b)-Os(1)-Os(2) 54.2(3), C(12)-Os(1)-Os(3) 118.8(3), Os(2)-Os(1)-Os(3) 60.55(8), C(22)-Os(2)-Os(1) 109.9(3), C(3b)-Os(2)-Os(1) 47.8(2), C(23)-Os(2)-Os(3) 93.1(3), C(4b)-Os(2)-Os(3) 74.4(3), Os(1)-Os(2)-Os(3) 63.48(9), C(33)-Os(3)-Os(2) 94.0(3), C(3a)-Os(3)-Os(2) 66.5(2), C(32)-Os(3)-Os(1) 113.5(4), C(4a)-Os(3)-Os(1) 91.6(3), Os(2)-Os(3)-Os(1) 55.97(7), C(4a)-C(3a)-C(4b) 124.1(10), C(3b)-C(4b)-C(3a) 126.6(9), C(3a)-C(4b)-C(5b) 120.3(9).

The molecular structure of compound **33** consists of an irregular triangular arrangement of osmium atoms with metal-metal bond lengths of 2.76, 2.98 and 2.90Å. As had been previously indicated by the ^1H nmr spectrum, two acenaphthylene units are co-ordinated to the cluster core in an asymmetric fashion. It is interesting to note that whereas, ligand B has undergone a double C-H bond cleavage at the five membered ring, C-H bond cleavage in ligand A has occurred at only one of the ethylenic carbons and C(4a) has retained a proton. The acenaphthylene units have dimerised and are bonding through C(4b) and C(3a) with a carbon-carbon bond length of 1.49Å. Both ring systems are essentially planar forming a dihedral angle of 60.1° to each other. The $C_{24}H_{13}$ dimer is essentially a five electron donor forming one σ bond with Os(1) {Os-C 2.08Å} and two π-interactions with Os(2) and Os(3) {mean Os-C 2.35Å}. Nine carbonyl ligands are terminally bound three to each osmium atom. Although the hydride ligand has not been located directly, through the distribution of the carbonyl ligands and the lengthening of the Os(1)-Os(3) bond, it may be assumed to bridge this edge. The Os-Os-C(carbonyl) angles for the carbonyl groups adjacent to this edge are significantly wider (mean 116°) than for the carbonyls adjacent to the other two edges (mean 95.7°).

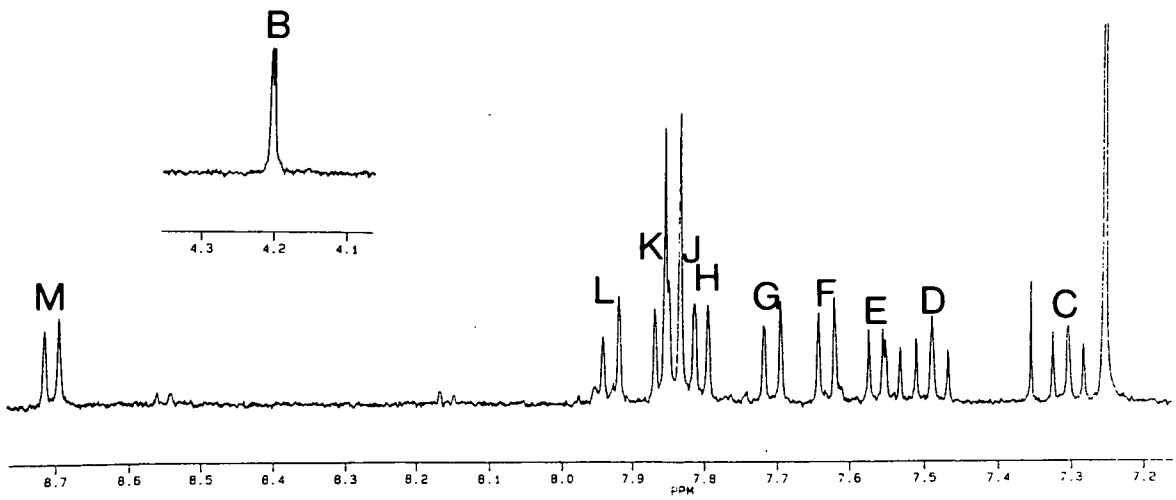

Figure 4.11: The ^1H nmr spectrum of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$33

The molecular structure of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** and a series of homonuclear/nOe nmr experiments have led to the partial assignment of the ^1H nmr spectrum as shown in Figure 4.11. The signal at δ 4.20 (B) can be ascribed to the ethylenic proton on the five membered ring. Signal E shows a coupling to both signals

H and G and these have been attributed to the protons in positions 6, 7 and 8 on ligand A. An nOe response between signal G and L led to the assignment of position 10 and coupling responses between signal J/K with L and M allow ring system A to be fully assigned. Ring system B has however proven harder to interpret . The triplet signals D and C are thought to be associated with the metallated side of the ligand and have been ascribed to positions 7 and 11. Signal C shows a coupling to signals F and K/J. Signal F must however be remote from the metal as it displays nOe responses to both signals C and J/K and has therefore been attributed to position 8/10. On this basis the remaining signals were assigned.

The mass spectrum of compound $Os_2(CO)_6(C_{12}H_6)_2$**34** exhibits a parent peak at 851(calc:-849) followed by the sequential loss of six carbonyl groups. Cluster breakdown has occurred and a dimeric osmium cluster has been produced. From the ^1H nmr spectrum it can be seen that the acenaphthylene ligands are symmetrically bound to the cluster core. Full assignment of the ^1H nmr spectrum of **34** has been achieved by a series of homonuclear decoupling/ nOe experiments and is depicted in Figure 4.12. The spectrum displays five signals at δ 8.54, 8.15, 7.94, 7.73 and 7.61 ppm with relative intensities 1:1:2:1:1. The triplet signals A and B can easily be assigned to positions 7 and 11. Signal A shows a coupling to both signals C and E, likewise signal B couples in a similar fashion to signals D and F. No nOe responses were observed between signals E and F and therefore they have been attributed to the protons at positions 6 and12.

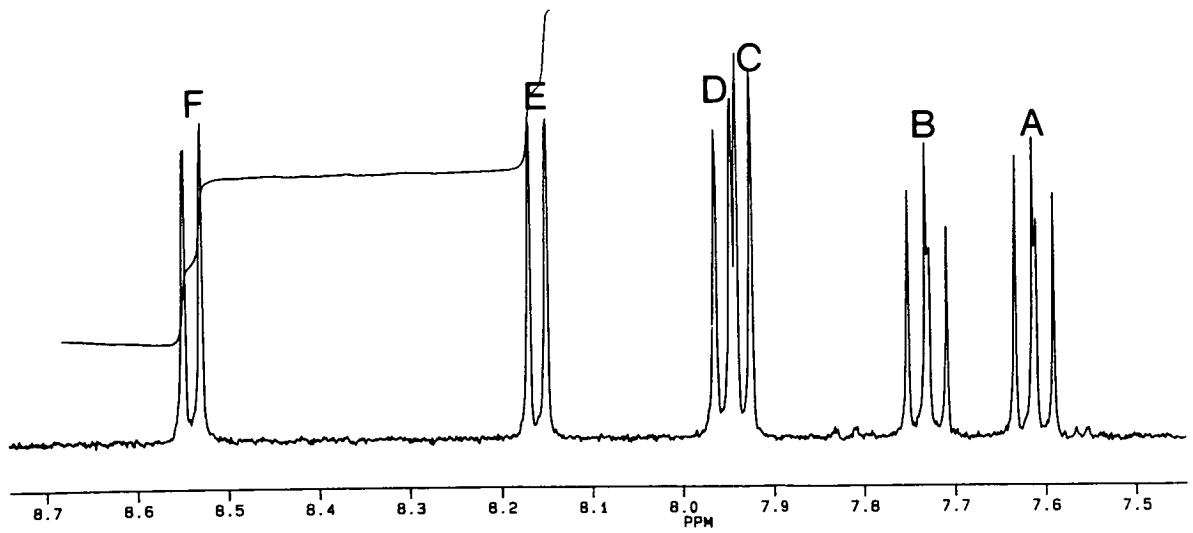

Figure 4.12: The ^1H nmr spectrum of $Os_2(CO)_6(C_{12}H_6)_2$**34**

The molecular structure of compound **34** has been established and is shown in Figure 4.13 together with some relevant bond lengths. Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation of a dichloromethane solution. The molecular structure of compound **34** consists of an osmium dimer with metal-metal bond length 2.75Å and two acenaphthylene units co-ordinated in a symmetrical fashion.

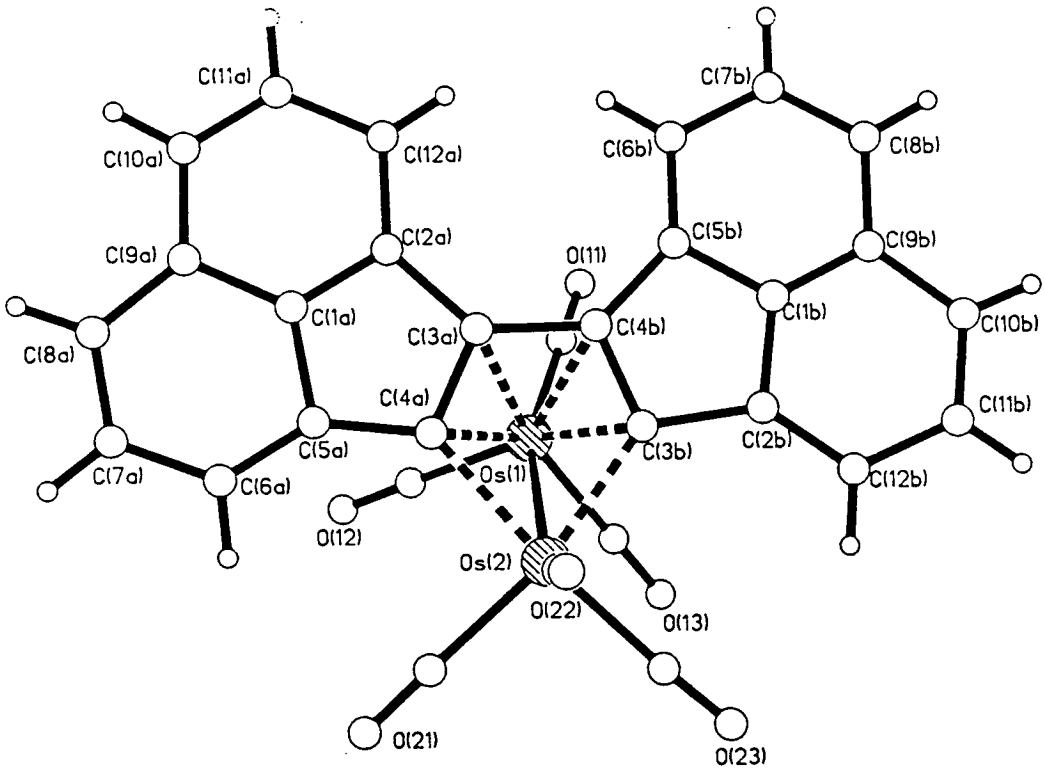

Figure 4.13: The solid-state molecular structure of $Os_2(CO)_6(C_{12}H_6)_2$**34**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å):-Os(1)-Os(2) 2.75(11), Os(1)-C(3b) 2.28(2), Os(1)-C(3a) 2.29(2), Os(1)-C(4b) 2.30(2), Os(1)-C(4a) 2.32(2), Os(2)-C(3b) 2.10(2), Os(2)-C(4a) 2.11(2), C(1a)-C(2a) 1.39(2), C(1a)-C(9a) 1.43(2), C(1a)-C(5a) 1.45(2), C(2a)-C(12a) 1.42(2), C(2a)-C(3a) 1.48(2), C(3a)-C(4a) 1.42(2), C(3a)-C(4b) 1.47(2), C(4a)-C(5a) 1.45(2), C(5a)-C(6a) 1.33(2), C(6a)-C(7a) 1.37(2), C(7a)-C(8a) 1.36(2), C(8a)-C(9a) 1.41(2), C(9a)-C(10a) 1.39(2), C(10a)-C(11a) 1.34(2), C(11a)-C(12a 1.43(2), C(1b)-C(5b) 1.39(2), C(1b)-C(9b) 1.40(2), C(1b)-C(2b) 1.41(2), C(2b)-C(12b) 1.35(2), C(2b)-C(3b) 1.52(2), C(3b)-C(4b) 1.38(2), C(4b)-C(5b) 1.46(2), C(5b)-C(6b) 1.38(2), C(6b)-C(7b) 1.42(2), C(7b)-C(8b) 1.38(2), C(8b)-C(9b) 1.42(2), C(9b)-C(10b) 1.44(2), C(10b)-C(11b) 1.36(2), C(11b)-C(12b 1.44(2), mean Os-C(CO) 1.92(2), mean C-O 1.12(2).

4.5 Some reactions of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** and $H_2Os_3(CO)_9(C_{12}H_6)$**31**

As demonstrated in the previous section, 4.4, the acenaphthylene ligand may undergo dimerisation with triosmium clusters at high temperatures. In order to ascertain when dimerisation occurs i.e. before or after one ligand has co-ordinated to the cluster core, an attempt was made to convert $H_2Os_3(CO)_9(C_{12}H_6)$**31** into $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33**. Thermal and photolytic activation of compound **31** in the presence of excess acenaphthylene ligand, result in the recovery of the starting compound $H_2Os_3(CO)_9(C_{12}H_6)$**31**. No evidence for dimerisation has been observed. It would therefore appear dimerisation does not occur while one ligand is already co-ordinated to the cluster core.

The compound $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** can be easily converted into the dimeric complex $Os_2(CO)_6(C_{12}H_6)_2$**34** when heated in nonane under reflux for 1 hour. This observation rationalises the increased yield of $Os_2(CO)_6(C_{12}H_6)_2$**34**, when the reaction of $Os_3(CO)_{12}$ **1** is carried out under reflux in nonane and a greater yield of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** when the reaction is carried out in octane.

4.6 Preparation of a mixed metal butterfly cluster

4.6.1 Ionic coupling

Ionic coupling reactions of carbonyl clusters to form higher nuclearity homo- and hetero-nuclear metallic systems have met with a varying degree of success. In the absence of a major redox or thermodynamic control, competition between alternative reactions and decomposition exists. In practice fragmentation, recombination or electron transfer may predominate.

The ionic coupling between the pentanuclear dianionic cluster $[Ru_5C(CO)_{14}]^{2-}$ and the cationic mononuclear benzene fragment $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ successfully affords the hexaruthenium benzene cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ in high yields.[43] In an attempt to extend this technique, the benzene cluster may be reduced (with loss of carbon monoxide) to produce the dianionic cluster $[Ru_6C(CO)_{13}(\eta^6\text{-}C_6H_6)]^{2-}$. However, treatment with a further aliquot of the cationic capping fragment $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ does not afford the heptaruthenium cluster that would be expected from such a reaction, but results in the introduction of a second benzene with the octahedral metal framework remaining intact. The benzene ligands both adopt different

co-ordination modes. One being η^6- terminally bound while the other spans a *triangulo* face in a μ_3-η^2:η^2:η^2 - fashion. Metal exchange has been observed by Shriver [44] in the reaction of $[Fe_3(CO)_{11}]^{2-}$ with $[Mn(CO)_3(MeCN)_3]^+$ where the major product isolated was the heterometallic compound $[Fe_2Mn(CO)_{11}]^-$.

Not all ionic coupling reactions prove to be successful, for instance, the reaction of $[Os_3(CO)_{11}]^{2-}$ with $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ results in the formation of $[Os_3(CO)_{12}]$ presumably by a process of oxidation and CO scavenging.[45] The high stability of neutral binary carbonyl clusters also predominates in the redox reactions of $[Os_6(CO)_{18}]$.[46]

It has been previously observed that alkyne ligands may stabilise cluster anions.[47] This fact was initially utilised in the synthesis of mixed metal butterfly systems and recently in the synthesis of tetra-osmium butterfly complexes containing a range of alkyne ligands. [48,49]

4.6.2 Preparation of $*CpRhOs_3(CO)_9(C_{12}H_6)$**36**

The compound $H_2Os_3(CO)_9(C_{12}H_6)$**31** exhibits a structure reminiscent of $H_2Os_3(CO)_9$(alkyne) clusters and it was envisaged that the reactivity of compound **31** may be very similar .

Compound **31**, when reduced by dropwise addition of a solution of potassium-benzophenone in distilled THF at room temperature, undergoes a colour change from yellow to deep orange. The anionic compound $[Os_3(CO)_9(C_{12}H_6)]^{2-}$ **35** is extremely moisture sensitive and due to it's instability has been characterised solely on the basis of IR spectroscopy. Reduction may similarly be carried out using the non-nucleophilic base DBU. Treatment of the dianion **35** with an equimolar quantity of $[*CpRh(MeCN)_3]^{2+}$ in dichloromethane at -78°C followed by the warming to room temperature affords one major product which can be separated by tlc using dichloromethane/hexane (3:7 v/v) as eluents. The compound was initially formulated on the basis of spectroscopic information as $*CpRhOs_3(CO)_9(C_{12}H_6)$**36**. The IR spectrum in the CO stretching region is concurrent with those of previously observed butterfly clusters. The mass spectrum exhibits a parent peak at 1210amu (calc:-1210) followed by the consecutive loss of at least nine carbonyl groups. A well resolved ^1H nmr spectrum could not be obtained. However a characteristic peak for the η^5- C_5Me_5 protons was observed at δ 1.24ppm.

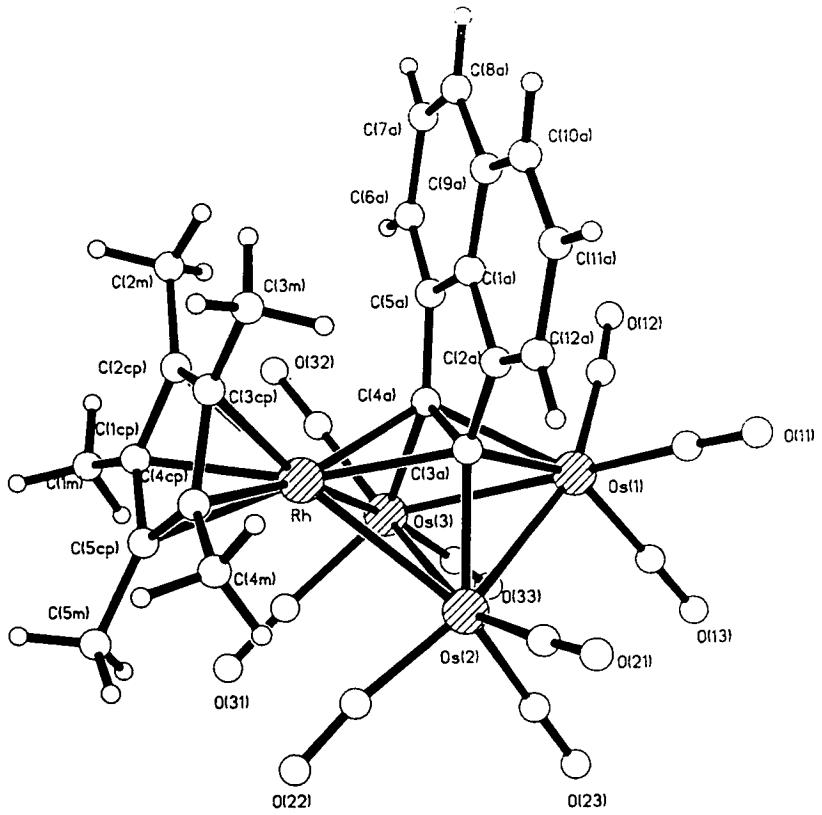

Figure 4.14: The solid-state molecular structure of $^{*}CpRhOs_3(CO)_9(C_{12}H_6)$**36**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths(Å): Os(1)-C(4A) 2.25(2), Os(1)-C(3A) 2.29(2), Os(1)-Os(2) 2.7551(12), Os(1)-Os(3) 2.7596(11), Os(2)-C(3A) 2.13(2), Os(2)-Rh 2.730(2), Os(2)-Os(3) 2.8901(13), Os(3)-C(4A) 2.14(2), Os(3)-Rh 2.691(2), Rh-C(4CP) 2.16(2), Rh-C(2CP) 2.18(2), Rh-C(4A) 2.19(2), Rh-C(3A) 2.19(2), Rh-C(1CP) 2.207(14), Rh-C(5CP) 2.218(14), Rh-C(3CP) 2.23(2), C(1A)-C(9A) 1.39(2), C(1A)-C(2A) 1.40(3), C(1A)-C(5A) 1.44(2), C(2A)-C(12A) 1.39(2), C(2A)-C(3A) 1.46(2), C(3A)-C(4A) 1.52(2), C(4A)-C(5A) 1.47(2), C(5A)-C(6A) 1.37(2), C(6A)-C(7A) 1.42(3), C(7A)-C(8A) 1.30(3), C(8A)-C(9A) 1.47(3), C(9A)-C(10A) 1.38(3), C(10A)-C(11A) 1.33(3), C(11A)-C(12A) 1.44(3), C(1CP)-C(5CP) 1.43(2), C(1CP)-C(2CP) 1.44(3), C(1CP)-C(1M) 1.45(2), C(2CP)-C(3CP) 1.46(3), C(2CP)-C(2M) 1.49(3), C(3CP)-C(4CP) 1.45(2), C(3CP)-C(3M) 1.45(3), C(4CP)-C(5CP) 1.45(2), C(4CP)-C(4M) 1.52(2), C(5CP)-C(5M) 1.47(2), C(1S)-C(2S) 1.39, C(1S)-C(6S) 1.39, C(2S)-C(7S) 1.39(4), C(2S)-C(3S) 1.39, C(3S)-C(4S) 1.39, C(4S)-C(5S) 1.39, C(5S)-C(6S) 1.39. Mean Os-C(CO) 1.90(2), mean C-O 1.15.

Crystals suitable for single crystal X-ray analysis were obtained from a toluene solution at -30°C. The molecular structure of $^{*}CpRhOs_3(CO)_9(C_{12}H_6)$**36** is depicted in Figure 4.14 together with relevant bond lengths and angles. The four metal atoms are arranged in a butterfly geometry with the rhodium atom occupying a "wing-tip" position. Nine carbonyl ligands were located, three bonded to each of the osmium

atoms. The *Cp ligand is η^5- bound to the rhodium atom. The acenaphthylene ligand forms two σ bonds with the two "hinge" osmium atoms and two π interactions with the "wing-tip" atoms. The two σ bonds are essentially symmetric with metal carbon lengths of 2.13 and 2.14Å, but the acenaphthylene ligand leans towards the Rh atom with the M-C-C bond lengths being 0.09Å shorter. The dihedral angle between the two wings of the butterfly is 114.4° which is consistent with the angle found in previously reported butterfly clusters. The *Cp ligand and the acenaphthylene act as a five and four electron donor respectively, this allows the cluster to achieve an overall electron count of 62, which is consistent with the M_4C_2 quasi-octahedral geometry expected by Wade's rules.

The reaction of the dianion $[Os_3(CO)_9(C_{12}H_6)]^{2-}$ **35** with equimolar quantities of the capping reagent $(C_6H_6)Ru(MeCN)_3^{2+}$ has also been attempted. However, no mixed metal butterfly cluster has been isolated in this case and recovery of the compound $H_2Os_3(CO)_9(C_{12}H_6)]^{2-}$ **35** is observed.

4.7 Concluding remarks

The objective at the onset of this work was to co-ordinate large polycyclic ring systems to trinuclear carbonyl clusters. The successful synthesis of $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$**30** demonstrates the ability of a large polycyclic moiety to adopt a face-capping co-ordination mode. Reactions could be carried out on the ligand while attached to the metal framework. The cluster may be able to stabilise an otherwise unstable species, allowing novel organic chemistry to be undertaken. The facile displacement of ligand from the cluster may provide a useful route to otherwise unattainable organic compounds. Nagashima[24] has utilised this approach and successfully hydrogenated the acenaphthylene ligand at the six membered ring, isolating a new dihydroacenaphthylene ring system.

The reaction of $Os_3(CO)_{12}$**1** with acenaphthylene to yield a variety of products, highlights the reactivity differences between osmium and ruthenium carbonyl clusters. The major product isolated $H_2Os_3(CO)_9(C_{12}H_6)$**31**, contains an acenaphthylene fragment that has undergone C-H bond cleavage at the five membered ring and is bound to the cluster in a benzyne fashion. As a result of C-H bond cleavage, dimeric acenaphthylene species have been observed and successfully co-ordinate to the cluster core. This may again provide a useful alternative method for synthesising larger polycyclic systems. However, displacement of the ligand from the triosmium cluster may prove difficult. From the results obtained so far, it would appear that a vast area of chemistry remains to be explored.

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Chapter 5: Experimental

5.1 General experimental procedures and instrumentation

Synthesis

All experiments were carried out under an atmosphere of nitrogen, using freshly distilled solvents, unless otherwise stated. Autoclave reactions were carried out in a magnetically stirred Burghoff(250 ml) autoclave fitted with a PTFE liner. $Ru_3(CO)_{12}$ and $Ru_6C(CO)_{17}$ were prepared by the literature methods,[1] while $Os_3(CO)_{12}$ was supplied by Oxchem Chemicals. $Os_3(CO)_{10}(MeCN)_2$ was prepared by the published method[2] and used without further purification. Trimethyl amine-N-oxide (Me_3NO), purchased as the dihydrate was dried initially by a Dean and Stark distillation in benzene and sublimed immediately prior to use. All other reagents were used as supplied without further purification unless stated otherwise.

Separations

All separations were achieved chromatographically on silica. Thin layer chromatography (tlc) was carried out using plates supplied by Merck with a 0.25mm layer of Merck Kieselgel 60 F_{254} . Column chromatography was carried out using a 50cm (2cm id) glass column with 60 mesh silica gel. Eluents were mixed from standard grade laboratory solvents.

Infrared spectroscopy

Infrared spectra were recorded in dichloromethane (unless stated to the contrary) on a Perkin-Elmer 1600 series fourier transform instrument, calibrated with carbon monoxide using NaCl cells (0.1mm path length).

Mass spectroscopy

Fast atom bombardment mass spectra were obtained on a Kratos MS50TC spectrometer using CsI as calibrant. Samples were dissolved in the minimum dichloromethane prior to addition of the matrix liquid.

NMR spectroscopy

^1H nmr spectra and ^{13}C nmr spectra were recorded on Bruker WH 200, 250 and AM 360 fourier transform instruments. In most instances spectra were recorded in deuterated chloroform ($CDCl_3$).

Single crystal X-ray diffraction analysis

Diffraction data were collected on an Enraf-Nonius CAD-4 or Stöe-Stadi-4-circle diffractometer. An Oxford Cryosystems device was used for data collection at low temperature. All structures were solved by Direct methods and refined by Full matrix least squares on F_{obs}^2 using computer programs Shelxs-86[3] and Shelxl-93[4]. The appropriate crystal data, data collection and structure refinement parameters are presented in the text.

5.2 Experimental details for chapter 2

Preparation of $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$4

The compound $HOs_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$ was prepared by the following modification of the literature procedure.[6] 1,3 cyclohexadiene(1.5 ml) was added to a solution of $H_2Os_3(CO)_{10}$(500 mg) in octane(100 ml) and the mixture heated under reflux at 125°C for 50 minutes. The solvent was removed *in vacuo* and the resulting residue extracted with dichloromethane(20 ml). The compound $HOs_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$ was used without further purification and heated with $[Ph_3C]^+[BF_4]^-$ (600 mg) in dichloromethane(20 ml) under reflux for 30 minutes. After the reaction was cooled to room temperature pale yellow microcrystals of $[HOs_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]^+[BF_4]^-$ were filtered and washed with dichloromethane(10 ml) and hexane(10 ml). The cationic benzene complex was then suspended in dichloromethane(60 ml) and stirred for 20 minutes with DBU to give a pale yellow solution. The solvent was removed *in vacuo* and purification by tlc using dichloromethane/hexane (3:7 v/v) as eluents afforded one major product characterised as $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$**4** (220 mg).

Spectroscopic data for compound **4**
IR cm^{-1} (υCO):-2076m, 2030vs, 1999m, 1978m, 1951sh
^1H nmr(CD_2Cl_2) δ:- 4.42s(6H)
MS(FAB):- 902 amu (calc:- 900)

Preparation of $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$6

The compound $Os_3(CO)_{10}(MeCN)_2$**3** (450 mg) was dissolved in dichloromethane (100 ml) and 1,3 cyclohexadiene (1.5 ml) was added. The reaction mixture was stirred for 1 hour at room temperature. The solvent was removed *in vacuo* and purification by tlc using dichloromethane/hexane (3:7 v/v) as eluents. One major yellow product was

obtained and characterised as $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** (400 mg). Crystals suitable for X-ray analysis were obtained from a toluene solution at 5°C.

Spectroscopic data for compound **6**
IR cm^{-1} (υCO):- 2110m, 2060s, 2023s, 2004m, 1975sh
^1H nmr($CDCl_3$) δ:-5.27m(2H), 3.77m(2H), 1.86m(4H)
MS(FAB):- 928 amu (calc:-930)
Crystal Data:- $C_{16}H_8O_{10}Os_3.C_2H_3N$, M=971.8, monoclinic, space group P21/n, a=8.932(8), b=17.387(13), c=14.833(15)Å, α=101.63(6), β=105.69(6), U=2218Å^3, Z=4, D_c=2.910 mg/m^3, F(000)=1736, crystal size 0.97 x 0.66 x 0.39mm , T=150 K, R1=0.044[2381 reflections with $F^\circ > 4\sigma(F^\circ)$], wR2=0.0861 for 3013 independent reflections, corrected for absorption and 149 parameters. Difabs[5] were applied at isotropic convergence (min 0.788, max 1.402). A region of disorder was resolved into two partly overlying MeCN solvates, each of which is half occupied.

Alternative preparation of $HOs_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$

The compound $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** (200 mg) was heated in octane(100 ml) under reflux at 125°C for 4 hours. The solvent was removed *in vacuo* and the remaining residue extracted with dichloromethane. Separation of the products by tlc eluting with dichloromethane/hexane (3:7 v/v) afforded 3 major products. The products were characterised in order of elution as $H_2Os_3(CO)_{10}$(15 mg), $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$**6** (100 mg) and $HOs_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$ (12 mg). Some cluster decomposition was also observed.

Reaction of $Ru_3(CO)_{12}$2 with Me_3NO and 1,3 cyclohexadiene

The compound $Ru_3(CO)_{12}$**2** (250 mg) was dissolved in dichloromethane (250 ml) and 1,3 cyclohexadiene(1.5 ml). The reaction mixture was cooled to -78°C and a solution of Me_3NO (94 mg, 3.2 mol. equiv.) in dichloromethane (20 ml) was added dropwise over a period of 5 minutes. The reaction mixture was stirred at room temperature for 1 hour. The solvent was removed *in vacuo* and the products separated by tlc eluting with dichloromethane/hexane (3:7 v/v). Two major products were isolated and characterised as $HRu_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$(63 mg) and $Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$5(40 mg).

The above reaction was repeated using benzene as solvent in place of dichloromethane and the yields of both compounds increased. $HRu_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$(89 mg) and $Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$5(60 mg).

Spectroscopic data for compound **5**

IR cm^{-1} (υCO):- 2071m, 2028vs, 1996m, 1985sh, 1976w

^1H nmr($CDCl_3$) δ:- 4.52s (6H)

MS(FAB):- 633 amu (calc:-633)

Conversion of $HRu_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$ into $Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$5

The compound $HRu_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)$(50 mg) was dissolved in hexane (100 ml) and heated under reflux for 3 hours. The reaction was monitored by IR spectroscopy to ensure the complete conversion of the starting material. The solvent was removed *in vacuo* and purification by tlc yielded the compound $Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$5(16 mg).

Reaction of $Os_3(CO)_{12}$1 with Me_3NO and 1,3 cyclohexadiene

The compound $Os_3(CO)_{12}$1(100 mg) was dissolved in dichloromethane(100 ml) and 1,3 cyclohexadiene(1.5 ml). The reaction mixture was cooled to 0°C and a solution of Me_3NO(25 mg, 3.2 mol. equivs.) in dichloromethane(4 ml) was added dropwise over a period of 5 minutes. The reaction was stirred at room temperature for 2 hours. The solvent was removed *in vacuo* and the products separated by tlc eluting with dichloromethane/hexane (3:7 v/v). Three yellow products were obtained and characterised in order of elution as $Os_3(CO)_{12}$1(50 mg), $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$6(4 mg) and $HOs_3(CO)_{10}Cl$ (7 mg).

General procedure for Birch reductions

The appropriate arene(25g), ^{t}BuOH(3 mol. equivs.) and THF(to effect dissolution, 75 ml) were added to a 3-necked 1 litre flask containing liquid ammonia(approx 400 ml). Lithium metal (4.3 mol. equivs.) was added slowly in small portions, initially the blue colour formed faded slowly as the reaction progressed, however, the blue colour persisted as an excess of lithium was added. The reaction mixture was stirred vigorously for a further 4 hours, then slowly quenched by the slow addition of MeOH(100 ml) until the solution was decolourised, water(100 ml) was then added and the ammonia allowed to evaporate slowly overnight. More water was added to dissolve precipitated salts and in addition pentane(50 ml) was added. The organic layer was removed and washed twice with water before drying over sodium sulphate(anhydrous). The solvent was removed *in vacuo* and the resulting 1,4 cyclohexadiene obtained as a pale yellow liquid.

Birch reduction of 1,2 diphenylethane

The compound 1,2 diphenylethane(4.557g), ^{t}BuOH(11.2g) and THF(100 ml) were added to a 3-necked 1 litre flask containing liquid ammonia(approx. 400 ml). Lithium metal (1.388g) was added slowly in small portions. The reaction was then carried out as described above. Final removal of the solvent *in vacuo* afforded a white crystalline product.

^{1}H nmr($CDCl_3$) δ:- 2.07s(4H), 2.64m(8H), 5.43s(2H), 5.70m(4H)

^{13}C nmr(CD_2Cl_2) δ:- 26.7(2C), 29.0(2C), 35.4(2C) {CH_2}, 118.2(2C), 124.2(4C) {CH}, 134.9(2C) {C}

Isomerisation of 1,4 cyclohexadienes to 1,3 cyclohexadienes

The appropriate 1,4 cyclohexadiene(5 ml) was heated under reflux in di-butyl ether(100 ml) with $Fe(CO)_5$(10 ml) for 24 hours. The cooled solution was filtered through silica to remove particles of iron (CAUTION, Pyrophoric) to yield a yellow solution. The solvent was removed *in vacuo* to yield a yellow oil.

Spectroscopic data for $Fe(CO)_3$(*o*-$Me_2C_6H_6$)**7**

IR cm^{-1} (υCO):- 2041vs, 1975vs, 1966vs

^{1}H nmr δ:- 1.58m (2H), 1.65s(3H), 1.80m(2H), 2.13s(3H), 2.94m(1H), 5.10d(1H)

^{13}C nmr δ:- 18.4, 23.0 {CH_3}, 24.8, 31.3 {CH_2}, 57.7, 83.2 {CH}, 77.8, 102.5 {C}, 212.8 {CO}

MS(EI):- 248 amu (calc:-248)

Spectrocopic data for $Fe(CO)_3$(*p*-$Me_2C_6H_6$)**9**

IR cm^{-1} (υCO):- 2042vs, 1975vs, 1966vs

^{1}H nmr δ:- Spectrum could not be obtained

^{13}C nmr δ:- Showed compound to be a complex mixture of isomers

MS(EI):- 248 amu(calc:-248)

Spectrocopic data for $Fe(CO)_3$(*m*-$Me_2C_6H_6$)**11**

IR cm^{-1} (υCO):- 2042vs, 1972vs

^{13}C nmr δ:- Complex mixture of isomers

MS(EI):- 250 amu(calc:- 248)

Spectrocopic data for $Fe(CO)_3(MeC_6H_7)$**13**

IR cm^{-1} (υCO):- 2044vs, 1772vs

MS(EI):- 234 amu (calc:-234)

Spectrocopic data for $Fe_2(CO)_6(C_{14}H_{18})$**15**

IR cm^{-1} (υCO):- 2045vs, 1982vs, 1974vs

^1H nmr δ:- 1.53-1.74m, 2.43-2.60m, 3.10dd, 5.21d

^{13}C nmr δ:- 23.6, 24.7, 39.5 {CH_2}, 59.2, 64.9, 85.5 {CH}, 105.1 {C}, 212.0 {CO}

MS(FAB):- 466 amu (calc:-466)

Disengagement of organic ligands from Iron complexes

The appropriate $Fe(CO)_3$(diene) (2g) was stirred with a saturated solution of Cupric chloride in methanol(100 ml) at room temperature overnight. The resulting green solution was extracted with hexane and the combined extracts washed with water, then dried over sodium sulphate(anhydrous). The solvent was removed *in vacuo* and an extremely pungent yellow oil obtained. This method proved extremely messy and an alternative was suggested

The appropriate $Fe(CO)_3$(diene) (2g) was dissolved in pentane(50 ml) and shaken vigourously with cerium(IV) ammonium nitrate(1M; 50 ml portions) until evolution of carbon monoxide gas had ceased. The organic layer was washed with water and dried over sodium sulphate(anhydrous). The solvent was removed *in vacuo* and a pungent smelling yellow oil obtained.

Reaction of $Os_3(CO)_{10}(MeCN)_2$3 with substituted 1,3 cyclohexadienes

The compound $Os_3(CO)_{10}(MeCN)_2$3(100 mg) was dissolved in dichloromethane (100 ml) and the appropriate 1,3 cyclohexadiene(1 ml) added. The reaction mixture was stirred at room temperature for 4 hours. The solvent was removed *in vacuo* and the products purified by tlc eluting with dichloromethane/hexane (3:7 v/v). In all cases one major yellow product was obtained and characterised as $Os_3(CO)_{10}(\eta^4$-diene). The spectroscopic data is listed below:

Spectroscopic data for $Os_3(CO)_{10}(\eta^4$-*o*-$Me_2C_6H_6)$**8**

IR cm^{-1} (υCO)(pentane):- 2110m, 2062vs, 2032vs, 2023vs, 2010s, 1991w, 1982m, 1967w

^1H nmr δ:- 1.72m (2H), 1.87s(3H), 2.01m(2H), 2.33s(3H), 3.35dt(1H), 6.11d(1H)

^{13}C nmr δ:- 17.7, 23.9 {CH_3}, 25.1, 30.4 {CH_2}, 56.4, 87.5 {CH}, 63.4, 91.5 {C}, 184.9 {CO}

MS(FAB):- 964 amu (calc:-959)

Spectroscopic data for $Os_3(CO)_{10}(\eta^4$-*p*-$Me_2C_6H_6)$**10**

IR cm^{-1} (υCO)(pentane):- 2111m, 2062vs, 2032vs, 2023vs, 2011s, 1990w, 1982m, 1970w

^1H nmr δ:- 0.96d(3H), 1.54m(1H), 2.03m(1H), 2.35s(3H), 2.37td(1H), 3.30dd(1H), 3.68dt(1H), 6.20dd(1H)

^{13}C nmr δ:- 20.96, 26.02 {CH_3}, 29.70 {CH_2}, 31.85, 34.22, 48.13, 64.52 {CH}, 89.01 {C}, 184.8 {CO}

MS(FAB):- 964 amu (calc:-959)

Spectroscopic data for $Os_3(CO)_{10}(\eta^4$-*m*-$Me_2C_6H_6)$**12**

IR cm^{-1} (υCO)(pentane):- 2110s, 2062vs, 2031vs, 2022vs, 2007vs, 1990w, 1981m, 1972w

^1H nmr δ:- 0.97d(3H), 1.54m(1H), 1.81s(3H), 2.21m(1H), 2.34m(1H), 3.54dd(1H), 4.92d(1H), 5.95m(1H)

^{13}C nmr δ:- 26.05, 26.92 {CH_3}, 33.32 {CH_2}, 38.00, 61.22, 68.65 {CH}, 73.14, 86.59 {C}

MS(FAB):- 961 amu (calc:-958)

Spectroscopic data for $Os_3(CO)_{10}(\eta^4$-$MeC_6H_7)$**14**

IR cm^{-1} (υCO)(pentane):- 2111m, 2062vs, 2032vs, 2024vs, 2010vs, 1990w, 1982m, 1974w

^1H nmr δ:- Complex mixture of isomers

MS(FAB):- 945 amu(calc:-944)

Reaction of $Os_3(CO)_{10}(MeCN)_2$3 with $C_{14}H_{18}$

The compound $Os_3(CO)_{10}(MeCN)_2$**3**(100 mg) was dissolved in dichloromethane (100 ml) and a solution of $C_{14}H_{18}$ (24 mg, 1.2 mol. equivs.) added. The reaction mixture was stirred at room temperature for 4 hours. The solvent was reduced *in vacuo* and the resulting residue filtered through a short silica column using hexane as eluent to remove any unreacted ligand. Further purification by tlc eluting with dichloromethane/hexane (1:9 v/v) mixture afforded two major products, one of which has been characterised as $Os_3(CO)_{10}(\eta^4$-$C_{14}H_{16})$**16** (20 mg).

Spectroscopic data for compound **16**

IR cm^{-1} (υCO)(pentane):- 2110m, 2062vs, 2032vs, 2024vs, 2011s, 1990w, 1982m, 1972w

^{1}H nmr δ:- 1.88m(1H), 2.02m(1H), 2.20m(2H), 2.41m(2H), 2.85m(2H), 3.68d(1H), 4.84d(1H), 6.02dd(1H), 7.11-7.32m(5H)
MS(FAB):- 1032 amu (calc:-1034)

5.3 Experimental details for chapter 3

Preparation of $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$(MeCN)17

The compound $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$**4** (50 mg) was dissolved in dichloromethane (5 ml) and the solution cooled to 0°C. A solution of Me_3NO (5 mg, 1.2 mol. equiv.) in acetonitrile (4 ml) was added dropwise over a period of 5 minutes. The solution was stirred for 15 minutes at room temperature, monitoring by IR spectroscopy , to ensure complete consumption of the starting material. The solvent was removed *in vacuo* and the resulting residue filtered through a short silica column eluting with dichloromethane. The yellow product $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$(MeCN)**17** (43 mg) was used without further purification.
IR cm^{-1}(MeCN) (υCO):- 2054s, 2012vs, 1985vs, 1971sh

Reaction of $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$(MeCN)17 with 1,3 cyclohexadiene

The compound $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$(MeCN)**17** (50 mg) was dissolved in dichloromethane (10 ml) and 1,3 cyclohexadiene (0.1 ml). The solution was stirred at room temperature for 1 hour. After this time IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and purification by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture afforded one major yellow band. The product was characterised as $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20** (41 mg).

Spectroscopic data for compound **20**
IR cm^{-1} (υCO):- 2063s, 2025vs, 1999s, 1984sh, 1957sh
^{1}H nmr δ:- 3.88br.s.(C_6H_6), 5.92m, 5.62m, 4.29m, 2.60m, 2.14m, 0.87m.
MS(FAB):- 952 amu (calc:-953)

Reaction of $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$20 with Me_3NO at room temperature

The compound $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20** (25 mg) was dissolved in dichloromethane (10 ml) and a solution of Me_3NO (2.4 mg, 1.2 mol. equiv.) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was stirred for 2 hours at room temperature, after which time some

decomposition was observed. IR spectroscopy indicated only starting material was present and no reaction had taken place.

Reaction of $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}C_6H_8)$20 with Me_3NO at 40°C

The compound $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}C_6H_8)$**20** (25 mg) was dissolved in dichloromethane (10 ml) and a solution of Me_3NO (2.4 mg, 1.2 mol. equiv.) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was heated to 40°C and stirred for 3 hours, after which time a colour change from yellow to orange was observed. The solvent was removed *in vacuo* and the residue separated by tlc using dichloromethane/hexane (3:7 v/v) as eluents. One yellow and one orange band were obtained and characterised as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^2{-}C_6H_8)$**20**(15 mg) starting material and $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)(\eta^4{-}C_6H_8)$**21**(6 mg) respectively. Single crystals suitable for X-ray analysis were obtained from a toluene solution of compound **21** at -30°C.

Spectroscopic data for compound **21**

IR cm^{-1} (υCO):- 2057s, 2016vs, 1985s, 1973sh, 1944sh.

^1H nmr(CD_2Cl_2) δ:- (296K) 4.28s (C_6H_6), 3.25 v br.s, 1.82d, 1.57d. (193K) 6.37(1H), 4.27 br.s(6H), 3.80(1H), 2.45(1H), 1.75(2H), 1.31(1H)

MS(FAB):- 927 amu(calc:-925)

Crystal Data:- $C_{19}H_{14}O_7Os_3$., M=924.90, triclinic, space group P-1, a=8.238(5), b=9.089(8), c=14.606(9)Å, α=101.63(6), β=92.00(5),γ=114.07(6), U=969.6(12)$Å^3$, Z=2, D_c=3.168 mg/m^3, F(000)=824, crystal size 0.50 x 0.38 x 0.35mm , T=150 K, 2.53<θ<25.00°, R1=0.029[3047 reflections with $F° > 4\sigma(F°)$], wR2=0.0861 for 3412 independent reflections, corrected for absorption and 262 parameters. Difabs[5] were applied at isotropic convergence (min 0.854, max 1.085)

Direct reaction of $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)$4 with Me_3NO and 1,3 cyclohexadiene

The compound $Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2{-}C_6H_6)$**4** (50 mg) was dissolved in dichloromethane (15 ml) and 1,3 cyclohexadiene (0.2 ml) and the solution cooled to -78°C. A solution of Me_3NO (15 mg, XS) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to reach room temperature and stirred for a further 1 hour. An obvious colour change to bright yellow was observed. The solvent was removed *in vacuo* and the residue separated by tlc eluting with dichloromethane/hexane (3:7 v/v). Two yellow bands were obtained in

approximately equal amounts and characterised as $Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)$**20** (13 mg) and $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$**22** (12 mg) respectively.

Spectroscopic data for compound **22**
IR cm^{-1} (υCO):- 2048s, 2000vs, 1986s, 1958sh, 1938sh
^1H nmr δ:- Spectrum could not be obtained
MS(FAB):- 927 amu (calc:-925)

Thermolysis of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$22

The compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$**22** (25 mg) was dissolved in dichloromethane (10 ml) and heated under reflux at 40°C for 4 hours. After which time a colour change from yellow to orange was observed and IR spectroscopy indicated complete consumption of the starting material. The solvent was removed under reduced pressure and separation by tlc eluting with dichloromethane/hexane (4:6 v/v) yielded two major products. Cluster decomposition was also observed The orange product was characterised as $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** (8 mg) and the yellow product as $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** (8 mg). Single crystals suitable for X-ray analysis were obtained from a toluene solution of compound **23** at -30°C.

Spectroscopic data for compound **23**
IR cm^{-1} (υCO):- 2092m, 2072vs, 2011vs.br.
^1H nmr(CD_2Cl_2) δ:- 7.51dd(1H), 7.48dd(1H), 6.97m(1H), 6.73m(1H), 4.82dd(1H), 4.20m(1H), 3.26m(1H), 1.82m(2H), 1.44m(2H), 0.79dd(1H), -16.32s(1H),-20.78d(1H)

MS(FAB):- 926 amu(calc:-925)
Crystal Data:- $C_{19}H_{12}O_7Os_3$., M=922.89, monoclinic, space group P21/n, a=8.883(3), b=14.473(7), c=16.148(8)Å, β=99.92(3), U=2042(2)$Å^3$, Z=4, D_c=2.998 mg/m^3, F(000)=1640, crystal size 0.17 x 0.17 x 0.17mm , T=150 K, $2.56<\theta<22.52°$, R1=0.0669[2034 reflections with $F° > 4\sigma(F°)$], wR2=0.1995 for 2660 independent reflections, corrected for absorption and 132 parameters. Difabs[5] were applied at isotropic convergence (min 0.833, max 0.131).

Photolysis of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$22

The compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_6H_8)$**22** (25 mg) was dissolved in toluene (10 ml) and cooled to 5°C. The solution was subjected to irradiation from a 500W tunsten-halogen heat lamp positioned 5cm from the reaction vessel for 1 hour.

After this time the solvent was removed *in vacuo* and separated by tlc eluting with a dichloromethane/hexane (4:6 v/v) mixture. Two major products were obtained and characterised by IR and ^{1}H nmr spectroscopy as $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** (10 mg) and $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** (10 mg).

Further reaction of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$21 with Me_3NO

The compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** (20 mg) was dissolved in dichloromethane(10 ml) and the solution cooled to -78°C. A solution of Me_3NO (1.9 mg, 1.2 mol. equiv.) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was stirred at room temperature for 1 hour, after which time extensive decomposition was observed. IR spectroscopy indicated only starting material was present and no reaction had taken place.

Reaction of $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$21 with trityl tetrafluoroborate

The compound $Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$**21** (20 mg) was dissolved in dichloromethane (<1 ml) and the solid $[Ph_3C]^+[BF_4]^-$ (50 mg, XS) added directly. The reaction mixture was stirred at room temperature for 20 minutes after which time an orange precipitate was observed. The product was filtered and washed with dichloromethane (5 ml) and hexane (10 ml) and formulated as $[Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$**25** (8 mg).

Spectroscopic data for compound **25**
IR cm^{-1} (υCO):- 2098s, 2049vs, 2018s, 1999sh
MS(FAB):- 923 amu(calc:-924)

Reaction of $[Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$25 with DBU

The compound $[Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$**25**(10 mg) was suspended in dichloromethane and the base DBU added slowly dropwise until a clear orange solution was obtained. The reaction mixture was stirred for a further 20 minutes. The solvent was removed *in vacuo* and the residue separated by tlc using dichloromethane/hexane (3:7 v/v) as eluents. One orange band was obtained and characterised as $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** (4 mg). Single crystals suitable for X-ray analysis were obtained from a toluene solution of compound **24** at -30°C.

Spectroscopic data for compound **24**
IR cm^{-1} (υCO):- 2038s, 2002vs, 1962sh, 1951sh, 1939sh

^{1}H nmr($CDCl_3$) δ:- 5.42s(6H), 3.97s(6H)
MS(FAB):- 896 amu(calc:-895)
Crystal Data:- $C_{18}H_{12}O_6Os_3.C_7H_8$, M=987.01, orthorhombic, space group $P2_12_12_1$, *a*=8.898(3), *b*=14.409(5), *c*=18.443(4)Å, U=2364.7(13)Å^3, Z=4, D_c=2.772 mg/m^3, *F*(000)=1784, crystal size 0.30 x 0.30 x 0.20mm, T=200K, 2.21<θ<24.96°, R1=0.0408[1959 reflections with $F^\circ > 4\sigma(F^\circ)$], wR2=0.0878 for 2363 independent reflections, corrected for absorption and 153 parameters.

Reaction of $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$23 with Me_3NO

The compound $H_2Os_3(CO)_7(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)$**23** (25 mg) was dissolved in dichloromethane (15 ml) and the solution cooled to -78°C. A solution of Me_3NO (2.5 mg, 1.2 mol. equiv.) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was stirred at room temperature for 1 hour, after which time a colour change from yellow to orange was observed. The solvent was removed *in vacuo* and separation by tlc eluting with dichloromethane/hexane (4:6 v/v) afforded one major product. The product was characterised as $H_2Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)(Me_3N)$**26** (18 mg). Single crystals suitable for X-ray analysis were obtained from a dichloromethane solution at -30°C.

Spectroscopic data for compound **26**
IR cm^{-1} (υCO):- 2072s, 2007vs, 1988sh, 1933br m
^{1}H nmr(CD_2Cl_2) δ:-7.43dd(1H), 7.15dd(1H), 6.78m(1H), 6.65m(1H), 4.92dd(1H), 4.20m(1H), 3.18m(1H), 3.06s(9H), 1.74m(2H), 1.38m(2H), 0.68dd(1H), -15.10s(1H),-17.46d(1H)
MS(FAB):- 957 amu(calc:-955)
CHN analysis(%):- Found C 26.97, H 2.19, N 1.43, Calc C 26.39, H 2.41, N 1.47
Crystal Data:- $C_{21}H_{21}NO_6Os_3$, M=953.01, monoclinic, space group $P2_1/n$, *a*=13.938(3), *b*=11.576(2), *c*=30.165(6)Å, U=4819.29(13)Å^3, Z=8, D_c=2.772 mg/m^3, *F*(000)=3464, T=200K, R1=0.0711[1730 reflections with $F^\circ > 4\sigma(F^\circ)$], wR2=0.1911 for 2371 independent reflections, corrected for absorption and 282 parameters.

Photolysis of $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$24

The compound $Os_3(CO)_6(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$**24** (10 mg) was dissolved in toluene (10 ml) and cooled to 5°C. The solution was subjected to irradiation from a 500W tungsten-halogen heat lamp positioned 5cm from the reaction vessel for 20 minutes, after which time extensive cluster decomposition had occured and no starting material could be recovered.

Reaction of $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)4$ with Me_3NO and 1,3 *ortho*-$Me_2C_6H_6$

The compound $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)4$ (50 mg) was dissolved in dichloromethane (15 ml) and 1,3 *o*-$Me_2C_6H_6$ (0.2 ml) and the solution cooled to -78°C. A solution of Me_3NO (15 mg, XS) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to reach room temperature and stirred for a further 1 hour. Extensive cluster decomposition was observed. The solvent was removed *in vacuo* and the residue separated by tlc eluting with dichloromethane/hexane (3:7 v/v). One yellow band was obtained and characterised as $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}o\text{-}Me_2C_6H_6)$**27**(10 mg).

Spectroscopic data for compound **27**
IR cm^{-1} (υCO):- 2064s, 2027vs, 1999s, 1989sh
^1H nmr δ:- Spectrum could not be obtained
MS(FAB):- 981 amu (calc:-980)

Reaction of $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)4$ with Me_3NO and 1,3 *para*-$Me_2C_6H_6$

The compound $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)4$ (50 mg) was dissolved in dichloromethane (15 ml) and 1,3 *o*-$Me_2C_6H_6$ (0.2 ml) and the solution cooled to -78°C. A solution of Me_3NO (15 mg, XS) in dichloromethane (2 ml) was added dropwise over a period of 5 minutes. The reaction mixture was allowed to reach room temperature and stirred for a further 1 hour. The solvent was removed *in vacuo* and the residue separated by tlc eluting with dichloromethane/hexane (3:7 v/v). Two products were obtained and characterised as $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}p\text{-}Me_2C_6H_8)$**28** (10 mg) and $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}p\text{-}Me_2C_6H_8)$**29** (5 mg) respectively.

Spectroscopic data for compound **28**
IR cm^{-1} (υCO):- 2064s, 2026vs, 2001s, 1988sh
^1H nmr δ:- Spectrum could not be obtained due to insufficient sample
MS(FAB):- 982 amu (calc:-980)

Spectroscopic data for compound **29**
IR cm^{-1} (υCO):- 2057s, 2016vs, 1986s, 1970sh, 1947sh
^1H nmr δ:- Spectrum could not be obtained due to insufficient sample
MS(FAB):- 954 amu (calc:-952)

5.4 Experimental details for chapter 4

Reaction of $Ru_3(CO)_{12}$2 with acenaphthylene

The compound $Ru_3(CO)_{12}$ **2** (250 mg) in octane (100 ml) containing an excess of acenaphthylene (150 mg) was heated under reflux at 125°C for 4 hours. After this time the reaction mixture had darkened to a deep red and IR spectroscopy indicated complete consumption of the starting material. The solvent was reduced *in vacuo* and the resulting residue filtered through a short silica column using hexane as eluent to removed any unreacted ligand. Further purification by tlc eluting with dichloromethane/hexane (3:7 v/v). The major red band was extracted and characterised as $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$**30**(200 mg). Crystals suitable for X-ray diffraction were grown from a solution of dichloromethane at -30°C.

Spectroscopic data for compound **30**

IR cm^{-1} (υCO):- 2043s, 2012vs, 1997s, 1958br

^1H nmr δ:- 6.50d(H6), 6.22dd(H11), 6.03d(H3), 5.81d(H12), 5.60t(H7), 5.51d(H10), 4.94d(H4), 2.60d(H8).

^{13}C NMR δ:- 128.3(C11), 114.0(C12), 96.8, 86.5, 82.7, 77.4(C1,C2,C5,C9), 79.3(C4), 76.1(C3), 66.2(C7), 65.1(C10), 63.2(C6), 35.5(C8).

MS(FAB):- 653 amu (calc:-651)

Crystal Data:- $C_{19}H_8O_7Ru_3.0.5(CH_2Cl_2)$, M=693.2, monoclinic, space group P2/n, a=20.080(7), b=9.262(3), c=20.337(8) Å, β=93.30(3), U=3776Å^3, Z=8, D_c=2.441 mg/m^3, F(000)=2648, crystal size 0.4 x 0.3 x 0.15, T= 150°K, 2.5 <θ<22.5°, R1=0.061[3619 reflections with $F^o > 4\sigma(F^o)$], wR2=0.0788 for 4563 independent reflections, corrected for absorption and 357 parameters.

Reaction of $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$30 with carbon monoxide

The compound $Ru_3(CO)_7(\mu_3{:}\eta^5{:}\eta^3{:}\eta^2\text{-}C_{12}H_8)$**30** (50 mg) was dissolved in dichloromethane (20 ml) and stirred at room temperature under an atmosphere of CO gas. After 15 minutes the dark red solution had turned yellow. The solvent was removed *in vacuo* and purification by tlc eluting with dichloromethane/hexane (4:6 v/v) One yellow and one orange product were obtained and characterised as $C_{12}H_8$(5 mg) and $Ru_3(CO)_{12}$2(20 mg) respectively.

Reaction of $Os_3(CO)_{10}(MeCN)_2$3 with acenaphthylene

The compound $Os_3(CO)_{10}(MeCN)_2$3(250 mg) was suspended in octane(100 ml) with $C_{12}H_8$(50 mg) and heated under reflux at 125°C for 2 hours.The solvent was

removed *in vacuo* and the residue separated by tlc using dichloromethane/hexane(4:6 v/v) as eluents. A range of products were obtained, the major yellow band was extracted and characterised as $H_2Os_3(CO)_9(C_{12}H_6)$**31**(100 mg). The other products were all in very low yields and were not characterised. Crystals suitable for X-ray diffraction were grown from a dichloromethane solution at 5°C.

Spectroscopic data for compound **31**
IR cm^{-1} (υCO):- 2110m, 2080s, 2056vs, 2034m, 2023sh, 2006m, 1980sh.
^1H nmr(CD_2Cl_2) δ:- 7.86d(1H), 7.82d(1H), 7.60m(4H), -18.96brs(2H)
MS(FAB):- 975 amu (calc:-974)
Crystal Data:- $C_{21}H_6O_9Os_3$., M=972.86, monoclinic, space group P21/n, a=10.472(3), b=18.845(9), c=11.146(4) Å, β=98.14(4), U=2177.4Å^3, Z=4, D_c=2.968 mg/m^3, F(000)=1728, crystal size 0.54x 0.54x 0.54mm , T=150 K, 2.72<θ<22.52°, R1=0.055[2589 reflections with $F° > 4\sigma(F°)$], wR2=0.1528 for 2845 independent reflections, corrected for absorption and 193 parameters.Difabs[5] were applied at isotropic convergence(min 0.770, max 1.299)

Reaction of $Os_3(CO)_{12}$1 with acenaphthylene

The compound $Os_3(CO)_{12}$**1** (200 mg) in nonane(30 ml) containing excess $C_{12}H_8$(150 mg) was heated under reflux at 152°C for 12 hours. The solvent was removed *in vacuo* and the residue taken up in dichloromethane and separated by tlc eluting with dichloromethane/hexane (2:8 v/v).A range of products were observed four of which have been characterised in order of elution as $H_2Os_3(CO)_9(C_{12}H_6)$**31**(65 mg), $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33**(25 mg) and $Os_2(CO)_6(C_{12}H_{24})_2$**34**(20 mg) and $Os_6(CO)_{18}$**32**(10 mg).Single crystals of compounds **33** and **35** suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution, in both cases. Single crystals of compound **32** were obtained from a deuterated chloroform solution at -30°C.

Spectroscopic data for $Os_6(CO)_{18}$**32**
IR cm^{-1} (υCO)(hexane):-2072s, 2059s, 2035s, 2028m, 2017w, 1999w
MS(FAB):- 1644 amu (calc:-1644)
Crystal Data:- $C_{18}O_{18}Os_6.CHCl_3$., M=1764.75, monoclinic, space group P21/n, a=10.074(3), b=27.293(9), c=11.286(3) Å, β=91.47(3), U=3102.1^3, Z=4, D_c=3.779 mg/m^3, crystal size 0.35x 0.31x 0.23mm , T=150 K, R1=0.036[3335 reflections with $F° > 4\sigma(F°)$], wR2=0.087 for 3855 independent reflections, corrected for absorption and 326 parameters.

Spectroscopic data for $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33**

IR cm^{-1} (υCO):- 2088s, 2064s, 2056sh, 2038vs, 2012brm

^1H nmr(CD_2Cl_2) δ:- -18.08s(1H), 4.20d(1H), 7.30t(1H), 7.49t(1H), 7.55dd(1H), 7.62d(1H), 7.71d(1H), 7.80d(1H), 7.85m(4H), 7.93d(1H), 8.70d(1H)

MS(FAB):- 1126 amu (calc:-1124)

Crystal Data:- $C_{33}H_{14}O_9Os_3$., M=1124.03, triclinic, space group P-1, a=7.527(6), b=12.065(13), c=16.62(2) Å, α=77.74(9), β=76.98(8), γ=77.08(8), U=1413$Å^3$, Z=2, D_c=2.643 mg/m^3, F(000)=1022, crystal size 0.35x 0.23x 0.08mm , T=150 K, $2.55<\theta<22.49°$, R1=0.0295[3230 reflections with $F° > 4\sigma(F°)$], wR2=0.0735 for 3672 independent reflections, corrected for absorption and 406 parameters.

Spectroscopic data for $Os_2(CO)_6(C_{12}H_6)_2$**34**

IR cm^{-1} (υCO):- 2078m, 2048vs, 2006sbr, 1966 mbr

^1H nmr(CD_2Cl_2) δ:- 7.61t(2H), 7.73t(2H), 7.94m(4H), 8.15d(2H), 8.54d(2H)

MS(FAB):- 851 amu (calc:-849)

Crystal Data:- $C_{30}H_{12}O_6Os_2$., M=848.80, monoclinic, space group P21/n, a=8.580(2), b=19.294(4), c=14.381(4) Å, β=100.96(2), U=2337.2$Å^3$, Z=4, D_c=2.412 mg/m^3, F(000)=1568, crystal size 0.23x 0.16x 0.10mm , T=150 K, $2.56<\theta<22.58°$, R1=0.0377[2409 reflections with $F° > 4\sigma(F°)$], wR2=0.1244 for 3065 independent reflections, corrected for absorption and 223 parameters.

Conversion of $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$33 into $Os_2(CO)_6(C_{24}H_{12})$34

The compound $HOs_3(CO)_9(C_{12}H_6)(C_{12}H_7)$**33** (20 mg) was heated in nonane under reflux at 152°C for 3 hours. The solvent was removed *in vacuo* and the residue purified by tlc using dichloromethane/hexane (3:7 v/v) as eluents. The major product was characterised by IR and ^1H nmr spectroscopy as $Os_2(CO)_6(C_{12}H_{24})_2$**34**(5 mg).

Reaction of $H_2Os_3(CO)_9(C_{12}H_6)$31 with acenaphthylene

The compound $H_2Os_3(CO)_9(C_{12}H_6)$**31** (25 mg) was suspended in octane (50 ml) with $C_{12}H_8$ (10mg) and heated under reflux at 125°C for 2 hours. The solvent was removed *in vacuo* and the residue separated by tlc using dichloromethane/hexane (4:6 v/v) as eluents. Two yellow products were obtained and characterised in order of elution as $C_{12}H_8$ (6 mg) and $H_2Os_3(CO)_9(C_{12}H_6)$**31** (17 mg).

The above reaction was repeated heating in nonane (50 ml) under reflux at 152°C for 2 hours. Extensive cluster decomposition was observed.

Photolysis of $H_2Os_3(CO)_9(C_{12}H_6)$31 with acenaphthylene

The compound $H_2Os_3(CO)_9(C_{12}H_6)$**31** (25 mg) and $C_{12}H_8$ (10 mg) were dissolved in toluene (10 ml) and cooled to 5°C. The solution was subjected to irradiation from a 500W tungsten-halogen heat lamp positioned 5 cm from the reaction vessel for 1 hour. After this time the solvent was removed *in vacuo* and separated by tlc eluting with a dichloromethane/hexane (3:7 v/v) mixture. Two yellow products were obtained and characterised in order of elution as $C_{12}H_8$ (8 mg) and $H_2Os_3(CO)_9(C_{12}H_6)$**31** (20 mg).

Reduction of $H_2Os_3(CO)_9(C_{12}H_6)$31

A solution of potassium-benzophenone was prepared by stirring potassium(150 mg) and benzophenone(700 mg) in freshly distilled THF(20 ml) for 2 hours at room temperature.

The compound $H_2Os_3(CO)_9(C_{12}H_6)$**31** (50 mg) was dissolved in freshly distilled THF (5 ml) and the deep blue potassium benzophenone solution was added dropwise, the yellow solution turned deep orange immediately. The reaction was monitored by IR spectroscopy, on completion the solvent was removed *in vacuo* to yield an orange oil.

Alternatively the compound $H_2Os_3(CO)_9(C_{12}H_6)$**31** was dissolved in freshly distilled THF(5 ml) and the base DBU added dropwise until all the starting material had been consumed, monitoring with IR spectroscopy.

Preparation of *$CpRhOs_3(CO)_9(C_{12}H_6)$ 36

The compound $[Os_3(CO)_9(C_{12}H_6)]^{2-}$**35** (40 mg) was dissolved in dichloromethane(5 ml) and the solution cooled to -78°C. A solution of $[*CpRh(MeCN)_3]^{2+}$**7** (25 mg) in MeCN (3 ml) was added dropwise, the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. The solvent was removed *in vacuo* and the resulting residue extracted with dichloromethane(2 ml). Separation of the products by tlc using dichloromethane/hexane (70:30) as eluents afforded a yellow and a red product characterised as $H_2Os_3(CO)_9(C_{12}H_6)$**31**(9 mg) and $*CpRhOs_3(CO)_9(C_{12}H_6)$ **36**(22 mg).

Spectroscopic data for compound **36**

IR cm^{-1} (υCO):- 2072m, 2030vs, 2011s.

^1H nmr(CD_2Cl_2) δ:- 1.24 s(15H), 7.3-7.5 (6H)

MS(FAB):- 1210 amu (calc:-1210)

Crystal Data:- $C_{31}H_{21}O_9Os_3Rh.C_7H_8$, M=1295.06, monoclinic, space group P21/a, a=17.838(9), b=9.999(4), c=20.003(5) Å, β=94.87(3), U=3555Å^3, Z=4, D_c=2.420 mg/m^3, F(000)=2376, crystal size 0.80x 0.50 x 0.25mm , T=150 K, $2.51<\theta<22.56°$,

R1=0.041[4168 reflections with $F^{\circ} > 4\sigma(F^{\circ})$], wR2=0.1071 for 4595 independent reflections, corrected for absorption and 413 parameters.

Reaction of $[Os_3(CO)_9(C_{12}H_6)]^{2-}$ 35 with $(C_6H_6)Ru(MeCN)_3^{2+}$

The compound $[Os_3(CO)_9(C_{12}H_6)]^{2-}$**35** (40 mg) was dissolved in dichloromethane(5 ml) and the solution cooled to -78°C. A solution of $[(C_6H_6)Ru(MeCN)_3]^{2+}$**8** (23 mg) in MeCN (3 ml) was added dropwise, the reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. The solvent was removed *in vacuo* and the resulting residue extracted with dichloromethane(2 ml). Separation of the products by tlc using dichloromethane/hexane (70:30) as eluents afforded one major product characterised as $H_2Os_3(CO)_9(C_{12}H_6)$**31**(14 mg).

5.5 References

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